This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

+ *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.

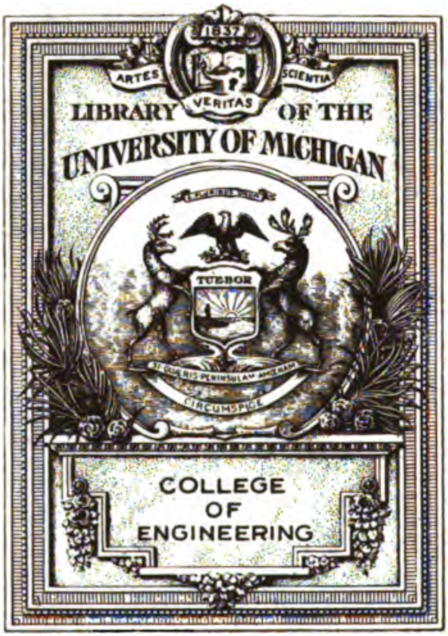
+ *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.

+ *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.

+ *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at `http://books.google.com/`


1837
ARTES
SCIENTIA
VERITAS
TUEBOR
E PLURIBUS UNUM
SI QUAERIS PENINSULAM AMOENAM
CIRCUMSPICE

TECHNOLOGY OF CELLULOSE ESTERS

A THEORETICAL AND PRACTICAL TREATISE ON THE ORIGIN,
HISTORY, CHEMISTRY, MANUFACTURE, TECHNICAL APPLICATION AND ANALYSIS OF THE PRODUCTS OF ACYLATION AND
ALKYLATION OF NORMAL AND MODIFIED CELLULOSE, INCLUDING NITROCELLULOSE, CELLULOID, PYROXYLIN, COLLODION,
CELLOIDIN, GUNCOTTON, ACETYLCELLULOSE AND VISCOSE,
AS APPLIED TO TECHNOLOGY, PHARMACY, MICROSCOPY,
MEDICINE, PHOTOGRAPHY, AND THE WARLIKE
AND PEACEFUL ARTS

IN TEN VOLUMES

BY

EDWARD CHAUNCEY WORDEN, PH.C., B.S., M.A., F.C.S.
AUTHOR "NITROCELLULOSE INDUSTRY"

VOLUME ONE—PART ONE

Cellulose Starch Cotton

London
E. & F. N. SPON, LTD., 57 HAYMARKET, S.W. 1
1921

To

Those co-workers

Who by Their Inspiration, Counsel and Material
Assistance Have Made its Preparation Possible
This Work, in Grateful Appreciation
is

Affectionately Dedicated

Work for the night
is coming, when
Man's work is done.

ANNOUNCEMENT

AND

PREFACE TO VOLUME ONE

The projected ten volumes constituting this series on the *Technology of Cellulose Esters*—of which Volume VIII on the Carbohydrate Carboxylates (Cellulose Acetate) issued in 1916—is the outgrowth and amplification of the author's 1239-page, 2-volume work on *Nitrocellulose Industry* published in 1911 which contained selections from the nitrocellulose art in general, and, so far as the author is aware, was the first and only attempt to correlate and publish a survey of the entire subject of the commercial utilization of the cellulose nitrates, both in the peaceful arts and the warlike fields. It was not free from defects due to a first edition, and otherwise. In the Preface to that work, the author invited criticisms and suggestions from his readers along lines of improving a possible future edition, but the response was so widespread and specific (communications from over 300 separate sources being received), as to justify the hope that an entirely new work along broad lines might be accepted appreciatively.

Be it monumental or otherwise—every effort of attempted merit has a definite aim. The aim of this work is to present the entire subject of the combinations of normal and modified cellulose with acidyl and alkyl radicals in such completeness, clarity, accuracy and detail, that inability to locate the information desired in the Collective Indices, will be trustworthy evidence that the matter sought was either ephemeral, irrelevant, inaccurate, non-existent or valueless.

The success, utility and perpetuity of any undertaking, be it literary or otherwise, primarily rests upon the solidity and breadth of the foundation upon which the superstructure is proposed to be erected. This Volume I is to be regarded as the *foundation* upon which the succeeding volumes are to be built and expanded, while Chapter XII herein may not inaptly be likened to the framework of the superstructure which it is hoped will follow.

Furthermore, every proposition of maximum utility must be self-contained. This is the reason and the explanation for the insertion herein in detail and extent—perhaps greater than has heretofore been published in any language—the subject matter of the basic materials entering into these topics, and represented by Cellulose, Starch, Cotton, Nitric and Sulfuric Acids, forming the subject matter of Parts One and Two of this volume. The value of so doing will be more obvious when judged in the perspective of the succeeding volumes. Some may say that this first volume in the series is so broad as to include much that is irrelevant, but this point has been very carefully considered, and bearing in mind the exceeding complexity and almost limitless possibilities of the entire art sought to be encompassed within these volumes, it is felt that such criticisms should perhaps be withheld until the work has been completed. On this point, the author is undoubtedly better informed than the reader, being conversant with the entire material to be incorporated in the succeeding volumes, and the sequence of presentation.

It is, of course, beyond human mentality to hope to completely encompass a given technical subject and register the multitudinous ramifications which have been recorded. To closely approach such an ideal also requires extensive finance for organization, library facilities, and long sustained mental perseverance. In the first of these requisites we are lacking; in the second, amply equipped by a private library containing full sets of the usual repositories of the science; and in the third, we hope, not strikingly deficient. This projected ten volume work, therefore, represents rather an attempt to circumscribe the subject with a completeness limited by the finances at our disposal, but with an earnest endeavor to record the subject in completeness, logical sequence and accuracy commensurate with the importance of the matter involved and its present activity and transitional state of development. Although realizing that conciseness is the essence of clarity, yet some ideas cannot be properly conveyed without a somewhat involved technique of utterance. Above all, it has continually been borne in mind that the statements are aimed at the intelligence of a sympathetic human being.

Unhasting and unresting, for nearly twenty-five years we have been accumulating significant material from every available source, and focussing our activities toward this *one* purpose—of recording in a permanent and readily available form, the rise, development and potentialities of this fundamental division of human progress. The data comprehending the entire series has now been arranged on some 365,000 cards.

While in no way attempting to perpetuate on paper every brain-wave which has afflicted the would-be inventor and literary aspirant, yet a work which aims at approaching completeness must not be bounded by the intellectual horizon alone of the author as including only those ideas, processes and products in which *he* may be able to perceive merit, for many a hazy idea and nebulous thought which has failed in the hands of one inventor, has been taken up in after years by those of clearer perception or more subtle intuition, and been made successful by the addition or omission of some seemingly unimportant detail. Therein lies the possible value and justification for the enumeration of those processes which *appear* to be capable of developing merit. The improvements in the entire cellulose ester art is an exemplification of the successes of one having been built upon the failures of another, for a knowledge of their failures is often of more importance than an acquaintance with their successes.

No attempt has been made to produce a work radically new, novel, different or revolutionary, but rather to approach the subject from the point of concrete analysis, logical deduction and historical continuity in development. In endeavoring to encompass such a broad subject with maximum clarity, all matter considered not strictly relevant has been relegated to the note (fine print) portion, as well as the more or less abstruse data for advanced thinkers.

An author can do little more than select that which the art has disclosed to him as being trustworthy, indicating the salient points, editing both sides of controversial questions, and interpreting them in the light of his personal knowledge. However, wherever his inferences are fallacious, his reasoning illogical, or his interpretation faulty, then his deductions may be distinctly harmful. But where the author has backed up his statements by references to the original literature, it then becomes possible for the student to refer to these repositories and draw an independent conclusion, and therein lies the value of original citations. In the amplification of these subjects, it seems as if the above idea had been carried out to a painstaking degree as indicated by the 80,504 references contained in this volume, and the more than 335,000 references in the work as a whole.

Erroneous deductions are often made of methods, ideas and processes which have not had the opportunity to mature under the mellowing perspective of elapsed time and therefore may be faulty, for it is true that until an art has had some years of commercial application, it is well nigh impossible to analyze and draw sound conclusions from the economics of the situation—the final arbiter in determining the social value of any process.

The attempt has been made to present the matter in as simple, terse, and lucid a manner as consistent with the intricacy of the subject involved, relying upon the references in the footnotes to furnish additional information to those particularly interested in a special topic.

Considerable thought and much attention has been given to the question of understandingly compressing the maximum of information into the minimum of space and bulk. Over 65% of this volume consists of fine print (notes), one page of which is equivalent (in ems) to 2.66 pages of text portion. The indices and prefatory portion are entirely in fine print. In this manner it has been possible to encompass the equivalent of 8700 pages of text into 3709 pages. Paper has been selected of thinnest super-stock compatible with proper wearing qualities, and in this manner the bulk (thickness and weight) have been reduced nearly a half over the usual.

The belief formerly held by us that the index was the most important part of a technical work has long since become a conviction, many an otherwise valuable book having been materially impaired by the omission, incompleteness, brevity or faulty construction of the index—in our judgment without question, the most important and painstaking portion of a work of this character. Recorded information remains practically valueless when rendered unavailable and inaccessible by omission in the index. In the 39,468 citations of 27,372 patents, 33,740 references to 23,542 separate names, and 20,370 entries under 20,601 subject headings, an earnest effort has been made to adequately cover the information recorded herein. However, it is obviously impossble without unwarranted expansion and useless repetition to correlate all the facts of one subject under a distinct heading, and therefore the indices should always be consulted in endeavoring to obtain the maximum of information upon a specified topic. The stupendous drudgery entailed in the indices preparation has been undertaken and superintended by Leo Rutstein, who also prepared the indices for Volume VIII of this series. Many dozens of temporary indices have we prepared of sections of this work during its progress, only to be discarded upon the completion of the section or chapter.

For convenience of handling and reference, it is proposed to divide the entire work into ten volumes paged separately, averaging about 1,000 pages per volume, with 108 chapters detailing the information under 3,340 topical headings and 6,775 sub-headings, and including 450 tables and 1,150 illustrations. The topics record the work of some 55,000 separate investigators, and include 58,000 patents. Each volume will close with patent, name and subject indices, Volume X being a collective index of the preceding volumes and including a formula index.

The plan of this volume is indicated on pages 1933, 2273, and 2377, comprehending 12 chapters, 637 topics, 3087 pages, 296 illustrations, 151 tables, and 19,611 notes in the text, and is divided as follows: *Part One.* The raw materials cellulose and its modifications (Chapter I), starch and similar carbohydrates (II), cotton as being the cellulose more often esterified (III), and the preparation of cotton for the esterifying process (IV). *Part Two.* Nitric acid is naturally divided into the five sections, (a) nitrogen and the five nitrogen oxides; (b) manufacture of nitric acid from niter and vitriol; (c) fixation of atmospheric nitrogen and the electrolytic manufacture of nitrogen oxides; (d) the catalytic manufacture of ammonia and its oxidation to nitric acid; (e) concentration, storage and analysis of nitric acid, all being Chapter V. Sulfur, sulfur dioxide and trioxide, and the mechanics and chemistry of the chamber, contact and other processes of sulfuric acid manufacture (VI). The physics, chemistry and analysis, rejuvenation, preparation and application of mixed and waste acids (VII). Physical constants, tables, and conversion factors involved in the preceding topics (VIII). *Part Three.* History and theory of the cellulose nitrates and nitrated carbohydrates, physical and chemical properties and ballistics (IX); manufacture of cellulose esters (X); analytical examination of nitrated carbohydrates (XI). *Part Four.* Synoptical development of the cellulose ester industry (XII). *Part Five.* Patent, Name and Subject Indices for the entire volume.

The general scope of the succeeding volumes is as follows: *Volume Two.* Vol. I closed with cellulose nitrate in the dry state and without commercial application, but inasmuch as the cellulose esters have comparatively few uses when dry, exhibiting their usefulness more forcibly when in solution either in the fluid or plastic state, Vol. II enumerates the cellulose ester solvents, non-solvents, ancillary bodies, activators, plasticizers, gelatinants and high-boilers, including fusel oil, alkyl and aryl esters, amyl alcohol and acetate, natural, artificial and synthetic camphor and the large number of bodies which have been proposed as adjuncts, accelerators, or substitutes for camphor in the cellulose ester thermoplastic arts. These solvents are largely used in the formation of paint and varnish removers, and in the preparation of substitutes for spirits of turpentine. The volume closes with the various processes for solvent recovery which have been proposed.

In respect to the data of which this Vol. II forms the subject matter, our progress has naturally been slow and laborious due to the immense amount of conflicting and contradictory information contained in the technical and patent literature, and to the time involved in endeavoring to check up this work ourselves in the laboratory, in order to be in a position to state authoritatively as to the real facts involved in the points at issue.

Volume Three. Having nitrocellulose (Vol. I) and the solvents (Vol. II), next comprizes an enumeration of the various appliances for bringing the two together for specific purposes—the transformation of the raw cellulose esters into finished products for employment in the arts. The manufacture and uses of the fluid pyroxylin preparations, lacquers, bronzing liquids, waterproofing solutions, enamels, impregnating media, the formation of artificial and imitation leather, coating of skins and hides with cellulose ester solutions are described and illustrated.

Volume Four. Those solutions which, when projected through capillary orifices into coagulating or hardening media result in the formation of filaments of artificial silk, broadly comprise the subject matter of this volume, and include the cuprammonium cellulose preparations, nitrocellulose silks, animal silks, and the entire subject of the commercial application of viscose, viscoid and the cellulose sulfocarbonates.

Volume Five. The entire subject of the history, chemistry, development, and ramification of the pyroxylin plastic industries typified by celluloid, xylonite and the various analogous products and substitutes, constitutes this volume, which probably will be issued in parts.

Volume Six. The multiplicity of uses to which collodion and other nitrated celluloses have been applied in pharmacy, botany, histology, pathology and especially photography, and including the industry of moving picture technique and continuous film formation, are involved in the volume.

Volume Seven. The higher cellulose nitrates, guncotton, the history, development, manufacture, application and composition of the various smokeless powders, gelatins, dynamites and all nitrocellulose-containing explosive preparations and guncotton combinations are embraced in this volume.

Volume Eight. The carbohydrate carboxylates (cellulose acetate), including the cellulose acetates, formates and other cellulose esters, the alkylated celluloses and acidylized derivatives, was published in 1916 as a 578-page volume, containing the citation of 3,272 patents, and 6,334 references in topical headings to the work of 1,292 investigators. This volume is under revision and considerable expansion.

Volume Nine, constitutes a Bibliography of Explosives, issued in parts, now in the press, exceeding 1,000 pages, and is being prepared under the able supervision of Dr. Carl Marx. This volume aims to separate the entire field of explosives into sectional topics, chronologically and alphabetically arranged, thus constituting a series of bibliographic monographs with abstract references, and copious indices.

Volume Ten. Patent, Name, Subject and Formulae Indices of the preceding nine volumes. The Collective Index.

It may be of interest to mention the existence of a series of collective indices of chemical patents of various countries which we have prepared as an aid to our work in the location, checking up and verification of patented processes, and which has been found exceedingly useful. We have examined page by page and have written on slips of paper all the patents where patent indices have not been published, or have photostatted them where printed, of *all* the patents mentioned in *complete* sets of the following journals for the periods indicated. Chem. Abst. 1907–1920; Jour. Amer. Chem. Soc. 1878–1920; Jour. Soc. Chem. Ind. 1882–1920; Jour. Chem. Soc. 1873–1920; Jour. Soc. Dyers & Col. 1881–1919; Arms & Expl. 1892–1920; Mon. Sci. 1857–1919; Bull. Soc. Chim. 1860–1919; Chem. et Ind. Jul. 1918–1920; Chem. Tech. Jahrb. 1881–1901; Wagner's Jahr. Chem. 1855–1918; Zts. ang. Chem. 1887–1920; Chemische Ind. 1878–1919; Ber. deut. Chem. Ges. 1874–1919; Chem. Ztg. 1879–1920; Chem. Tech. Repert. 1862–1900; Chem. Zentr. 1870–1920; Meyer Jahr. Chem. 1891–1918; Zts. Schiess. Sprengs. 1906–1920; Kunstoffe 1911–1920; Liebig-Kopp, Jahr. Chem. 1848–1910; Winther Organische Patent, 1877–1905; Friedländer, Teer Farbenfabriken, vols. I–XII.

The references thus obtained have been thrown in numerical order as to the patent numbers, typed, classified and the sheets thus obtained pasted in a series of large loose-leaf ledgers. In this manner we have available in a readily accessible form (all the U. S. patents, for instance, appearing in any of the above mentioned periodicals from 1,000 000–1,001,000, being located on the same page) over three million citations and abstracts of chemical patents. The labor involved in the preparation of this series of collective patent indices has been enormous, requiring the uninterrupted labor of four people for the past four and a half years. It is admitted that had we an adequate conception of the labor and cost involved before the work was commenced, it would not have been undertaken by us.

Those conversant with chemical literature research will recall that so often where the earlier encyclopedias and year books have happened to make an error in citation authors and bibliographers in succeeding years have copied the error without apparently taking the trouble to verify the accuracy of the reference or information by taking the time and trouble of consultation of the original repository. In this manner, inaccuracies appearing in such sets as Liebig-Kopp's Jahr. Chem. and Chem. Centr. have been accepted and transmitted verbatim through the works of succeeding years down to the present day, being copied from one work to another without verification. In contradistinction to the above, the author in at least 90% of the references contained herein, has verified the information from consultation of the *original* sources. It is unfortunate that the French in many instances content themselves with the prefix M. instead of the authors surname or initial, and that the English patent office practice puts forward the patent attorneys name in preference to that of the patentee, thus increasing the difficulty in according credit. It is but necessary to glance at the Index of Names in this volume to realize how essential it is that at least the initials of writers should always be given.

Many have been the gentlemen who have so willingly given of their time and mentality in contributing special topics to this volume, and if merit there be herein, to them in a large measure belongs the credit. Mr. Leo Rutstein, Dr. Carl Marx, and Messrs. DeWitt Bell, Clarence E. Lehmann, P. H. Bodenstein and John W. Bruce have constituted the staff responsible for the issuance of this volume.

Dr. Joseph Reilly has allowed us to draw upon his time and experience in elucidating abstruse points, and has contributed several of the topics. J. F. Briggs prepared the entire topic upon the analysis of cellulose (pp. 348–388), and is contributing to several of the more important portions of succeeding volumes. Professor J. R. Partington, M.B.E., D.Sc., of London University contributed the entire text portion of the Sulfuric Acid chapter with unimportant exceptions, from data supplied by the author. The completeness with which this subject has been handled by Professor Partington is indicated from the 6560 references in the several indices to this chapter. Professor E. J. Wall, F.R.P.S., has allowed us to draw from his life of experience in the broad subject of collodion as applied to photography, and has undertaken the preparation of substantially the entire text of one of the succeeding volumes. Dr. J. N. Goldsmith is engaged in arranging, writing, and editing the author's data upon the general subject of pyroxylin plastics.

It is a pleasure to acknowledge the unfailing courtesy of such firms as E. I. du Pont de Nemours & Co., New Explosives Co., and Nobel's Explosives Co., Ltd., and their technical staffs, for illustrations, manufacturing details and historical information. Especially have Messrs. Nobel's Explosives Co., and William Rintoul, O.B.E., F.I.C., prolifically contributed inaccessible data on the general subject of smokeless powder and nitrocellulose development and practice in Great Britain, much of the data being reserved for incorporation in Volume VII upon which we are actively engaged. Mr. F. W. Jones has also supplemented and amplified much of the above information from his expert knowledge and private archives of information. The Government of Great Britain through its several departments, with commendable broad-mindedness, has allowed the author to use information of great value. The English Patent Office Library—so far as the author's experience goes the most complete and readily accessible technical library in the world—has placed its facilities at our disposal, and Miss Nina Fovargue has been uninterruptedly engaged therein for the past two years in collating, collecting, amplifying and checking data for this work, and who is also responsible for the compilation of the entire Name Index.

Grateful appreciation is acknowledged to the Eschenbach Printing Co. and to Harvey F. Mack, the President, for the presswork of this volume, which must be conceded—with its 19,611 individual notes—as a difficult and intricate piece of typography, and especially to Miss Helen W. Smith, who furnished the nervous energy and administrative ability involved in the planning and execution of the printing. Mrs. E. S. Ketchledge did the proofreading.

The text is 10-point Ronaldson, and the notes 8-point Roman printed on 25″ x 38″, 70 lb. "olde Style" paper from monotype which was dismantled after the printing of each folio. The entire cost of the preparation, printing and publishing of this work has been met by the author personally, from his private funds.

Great care has been taken to record the various sources from which information has been drawn, and it is sincerely hoped that such sources have been duly acknowledged. The author would greatly appreciate suggestions and criticisms from readers of this work, with a view to extending its usefulness and increasing its accuracy in a possible future edition.

EDWARD CHAUNCEY WORDEN, FIRST.

MILBURN, NEW JERSEY,
October 15, 1920.

TABLE OF CONTENTS

This Table of Contents contains an enumeration of the 637 main topics only, the five hundred forty sub-topics not being indicated herein.

CHAPTER I.

CELLULOSE.

Carbohydrates.... 4
Classification of Celluloses.... 8
Constitution of Cellulose.... 14
Preparation of Pure Cellulose.. 26
Cellulose as a Colloid.... 30
Reactivity of Cellulose.... 36
Properties of the Celluloses.... 38
Viscosity of Cellulose Solutions 46
Optical Properties of Cellulose. 47
Cellulose and Heat.... 52
Action of Light and Air upon Cellulose.... 59
Absorption of Tannins by Cellulose.... 61
Cellulose and Dyestuffs.... 63
Cellulose Solvents.... 66
Action of Cuprammonium Solutions on Cellulose.... 68
Physical Constants of Cuprammonium Solutions.... 79
Application of the Cuprammonium Celluloses.... 85
Cellulose and Hydrochloric Acid.... 92
Cellulose and Sulfuric Acid.... 95
Action of Zinc Chloride on Cellulose.... 101
Vulcanized Fiber.... 104
Other Cellulose Solvents.... 106
Action of Salts on Cellulose.... 111
Acid Celluloses.... 122
Amyloid.... 125
Hydrocellulose.... 127
Action of Ozone on Cellulose... 151
Cellulose Peroxide.... 154
Cellulose and Oxidizing Agents. 158
Oxycellulose.... 164
Acetolysis and Octa-Acetylcellobiose.... 181
Hydrolysis and Saccharification 194
Cellulose Hydrates. Alkali Cellulose.... 213
Mercerization.... 224
Cellulose Condensations.... 234
Cellulose and Benzene.... 235
Cellulose and Phenol.... 236
Hemi-Celluloses.... 237
Ash.... 239
Producing Amorphous Cellulose for Subsequent Nitration.... 240
Lignocelluloses — (Jute and Wood).... 241
Wood Pulp.... 266
Wood Pulp for Esterification... 293
Cellulose Carbamates.... 324
Animal Celluloses.... 325
Esparto.... 327
Cellulose Filters.... 334
Cellulose Plastics and Aggregates.... 335
Pergamyn.... 337
Cellulith.... 338
Bacterial Action on Cellulose Materials.... 338
Analytical Examination of Cellulose Raw Materials.... 348
The Cellulose Complex.... 350
The Lignin Complex.... 353
The Cutin Complex.... 354
Alkaline Hydrolysis.... 356
Chlorination and Isolation of Ultimate Fibers.... 357
Examination of Cellulose Fibers 357
Moisture.... 358
Oil, Fat, Wax and Resin.... 359
Aqueous Extract.... 360
Alkaline Hydrolysis.... 361
Cellulose.... 362
Furfural Value or Pentosans.. 365
Methylpentosan.... 367
Acetic Acid Group.... 368
Methoxyl Group.... 368
Lignin.... 370
Chlorine Absorption.... 371
Phloroglucinol Absorption.... 371
Examination of Isolated Cellulose.... 372

Modified Cellulose.......... 377
Hydrated Cellulose.......... 377
Oxycellulose and Hydrocellulose 381
Viscosity.......... 385

CHAPTER II.

STARCH.

Origin and Transformation of Starch.......... 389
Occurrence of Starch.......... 405
Molecular Weight of Starch.... 406
Starch Iodide.......... 408
Starch Esters.......... 413
Action of Enzymes on Starch... 416
Formaldehyde and Starch..... 420
Starch and Heat.......... 422
Soluble and Modified Starch... 424
Microscopic Appearance of Starch.......... 433
Chemical Properties of Starch.. 433
Starch Paste.......... 441
Manufacture of Starch........ 445
Manufacture of Starch from Potatoes.......... 457
Rice Starch.......... 462
Corn Starch.......... 465
Action of Diastatic Ferments on Starch.......... 467
Action of Acids on Starch..... 475
Amylose.......... 481

CHAPTER III.

COTTON.

History of Cotton.......... 485
Botany of Cotton.......... 487
Microscopy of Cotton......... 497
Anatomical Structure of the Cotton Fiber.......... 501
Dimensions of Individual Cotton Fibers.......... 503
Moisture in Cotton.......... 508
Nitrogen in Cotton.......... 520
Mineral Constituents of Cotton 524
Tensile Strength of Cotton..... 527
Absorption of Gases by Cotton 529
Effect of Reagents on Cotton Fiber.......... 529
Composition of Cotton........ 530
Tissue Paper.......... 532
Cotton Wax.......... 534
Absorbent Cotton.......... 537
Methods of Cotton Analysis... 541
Tests of Cotton for Nitration Purposes.......... 552
Inspection of Cotton for Nitration Purposes.......... 552
U. S. Ordnance Requirements for Cotton.......... 554
English Requirements for Nitrating Cotton.......... 554
Specifications of Cotton for Nitration in Germany......... 555
Cellulose Used for Nitration... 555
Preparation of Cotton for Nitration.......... 560
The Utilization of Short Fibers 568
Cotton Hull Fibers.......... 579
Impurities in Cotton.......... 580
Cop Bottoms.......... 582

CHAPTER IV.

PREPARATION OF COTTON FOR ESTERIFICATION

Weight of Cotton Bales....... 583
Opening the Bale.......... 586
Boil-off.......... 588
Bleaching the Cotton......... 604
Preliminary Drying.......... 619
Teasing.......... 620
Willowing.......... 627
Conveying.......... 632
Final Drying.......... 634
Saco-Lowell Method of Cotton Preparation.......... 642
Treatment of Cotton for Esterification in Great Britain..... 644

CHAPTER V.

NITRIC ACID.

Historical.......... 665
Nitrogen.......... 679
Separation of Nitrogen from the Air.......... 684
Preparation of Pure Nitrogen.. 691
Properties of Nitrogen........ 691
Nitrogen Oxides.......... 693
Nitrogen Monoxide.......... 709
Nitrogen Dioxide.......... 712
Nitrogen Trioxide.......... 716
Nitrogen Tetroxide.......... 717
Nitrogen Pentoxide.......... 721
Manufacture of Nitric Acid with Chili Saltpeter.......... 722
Origin and Occurrence of Sodium Nitrate.......... 725
Formation and Composition of Chili Saltpeter.......... 728
Extraction and Purification of Chili Saltpeter.......... 728
Chili Saltpeter Statistics....... 731
Potassium Perchlorate........ 732
Analysis of Sodium Nitrate.... 732

Estimation of Nitrate in Chili Saltpeter 735
Recovery of Niter from Chili Saltpeter Bags 739
Manufacture of Nitric Acid from Sodium Nitrate 741
Manufacture of Nitric Acid from Chili Saltpeter in Great Britain 754
Nitric Acid Manufacture at Queen's Ferry Plant 773
The Commercial Utilization of Niter Cake 786
Hough Niter Cake Flaking Machine 808
Analysis of Niter Cake 810
The Manufacture of Nitric Acid and Caustic Soda Simultaneously 811
Other Nitric Acid Processes Using Metallic Nitrates 812
Uebel Nitric Acid Process 815
The Valentiner Vacuum Process for Making Nitric Acid 818
Hough Nitric Acid System 829
The Griesheim Nitric Acid Plant 834
Condensation of Nitric Acid 836
Condensing Nitric Acid by Means of Plate Towers 845
Continuous Nitric Acid Manufacture with Chili Saltpeter 845
Fixation of Atmospheric Nitrogen 847
Schönherr Process for Manufacturing Nitric Acid 853
K. Birkeland and S. Eyde Nitric Acid Process 869
Pauling Process of Nitric Acid Manufacture 881
Other Nitrogen Fixation Processes 892
Oxidation of Ammonia to Nitric Acid 894
Haber Method for the Synthetic Production of Ammonia 900
Badische Process for Synthetic Ammonia Formation 904
The Ostwald Process 911
Catalysts 915
Nitrides, Cyanides and Cyanamides as Sources of Nitric Acid 918
Nitric Acid from Nitrides 919
Cyanides and Cyanamides as Sources of Nitric Acid 925
Technical Production of Cyanamides 927
Other Processes for the Catalytic Production of Ammonia 934
Recovery of Nitric Acid from Various Sources 946
Recovery of Nitric Acid from Absorbents 948
Action of Nitric Acid on Aluminium 950
Properties of Nitric Acid 951
Storage and Transportation of Nitric Acid 955
Fuming Nitric Acid 960
Detection of Nitrous Acid 962
Detection of Nitric Acid 962
Determination of Nitrogen by Nitrometer 964
Determinations of Nitrogen by Lunge Two-Bulb Nitrometer 965
Determination of Nitrogen with the Gas-Volumeter 968
Determination of Nitrogen by du Pont Nitrometer 972
Estimation of Nitrogen by Ferrous Ammonium Sulfate 976
Determination of Nitric Acid in Niter Cake by Ferrous Ammonium Sulfate 978
Estimation of Nitrogen in Nitrocellulose by Ferrous Ammonium Sulfate 978
Determination of Nitric Acid by Nitron 979
Determination of Nitric Acid by Titration 981
Determination of Nitrous Acid by Permanganate 981
Manufacture of Absolute Nitric Acid 982
Refinement and Bleaching of Nitric Acid 984
Concentration of Nitric Acid 985

CHAPTER VI.

SULFURIC ACID.

History of Sulfuric Acid 1007
Sulfur 1011
Occurrence of Sulfur 1020
Sulfur in Sicily 1020
Sulfur in Louisiana and Texas 1023
Production of Sulfur from Sulfides 1024
Sulfur from Sulfates 1027
Sulfur from Sulfur Dioxide 1027
Sulfur from Alkali Waste 1028
Other Sources of Sulfur 1030
Sublimed Sulfur 1032
Properties of Sulfur 1034
Determination of Sulfur 1037

Pyrites 1043
Analysis of Pyrites 1046
Volumetric Analysis of Pyrites 1050
Gravimetric Analysis of Pyrites 1051
Sulfur Dioxide 1057
Sulfur Burners 1062
Sulfur Dioxide 1069
Pyrites Burners 1070
Sulfur Dioxide from Copper Pyrites 1075
Sulfur Dioxide from Blende 1076
Sulfur Dioxide from Galena 1081
The Composition of Burner Gases 1082
Sulfur Dioxide from Sulfates 1084
Other Sources of Sulfur Dioxide 1084
Absorption of Sulfur Dioxide 1087
Purification of Sulfur Dioxide 1089
Liquid Sulfur Dioxide 1092
Properties of Sulfur Dioxide 1094
Analysis of Sulfur Dioxide 1096
Uses of Sulfur Dioxide 1099
Sulfur Trioxide and Contact Sulfuric Acid 1100
Apparatus Used in the Contact Process 1106
Processes in the Contact Methods 1108
Platinum Catalysts 1113
Oxide of Iron Catalysts 1116
Chromium Catalysts 1119
Titanium Catalysts 1120
Vanadium Compounds 1120
Radioactive Catalysts 1121
Other Catalysts 1121
Electrical Processes 1122
Absorption of Sulfur Trioxide 1123
Properties of Sulfur Trioxide 1124
Analysis of Oleum 1126
Plant Tests 1127
Manufacture of Oleum from Sulfates 1128
Production of Oleum Other than by the Contact Process 1131
Theory of the Contact Process 1133
The Badische Process 1137
The Tentelew Process 1151
The Meister, Lucius and Brüning Process 1157
The Schroeder-Grillo Process 1161
Grillo Process at Queen's Ferry 1174
Preparation of Contact Mass for Grillo Plant 1183
The Freiburg Process 1189
The Rabe Process 1190
The Properties of Oleum 1191
Contact Processes in the United States 1191
Miscellaneous Contact Processes 1192
Lead Chamber Process of Sulfuric Acid Manufacture 1203
General Construction of the Lead Chamber 1205
The Erection of Lead Chamber 1207
Intensive Working of Chambers 1211
The Moritz Chambers 1212
The Niedenführ Chamber 1213
Falding's Chamber 1213
The Mills-Packard Chamber 1214
Tangential Chambers 1215
Intermediate Reaction Towers 1217
Replacement of the Lead Chamber by Other Apparatus 1222
The Opl System 1225
Chamber Fittings 1226
The Supply of Niter to the Chambers 1227
Water Supply of Chambers 1232
The Supply of Air to the Vitriol Chambers 1237
Anemometers 1240
Intensive Working and Reduction of Chamber Space 1242
Starting the Chamber Process 1244
Vitriol Chamber Temperatures 1245
Irregularities in Chamber Work 1246
Gas Distribution and Speed of Acid Formation 1247
Analysis of the Chamber Exit Gases 1252
Theory of the Lead Chamber Process 1254
Recovery of Nitrogen Compounds 1261
The Gay-Lussac Tower 1262
Tower Packing 1267
Distributing the Feed Acid 1272
Pumping the Acid 1274
The Glover Tower 1276
Recovery of Nitrogen Compounds 1284
Combined Chamber and Contact Process 1288
Various Processes for the Manufacture of Sulfuric Acid 1289
Pyrosulfuric Acid 1292
Persulfuric Acid and Persulfates 1293
Miscellaneous Methods for Sulfuric Acid Manufacture 1294
Sulfuric Acid from Sulfates 1299
Sulfuric Acid and Nitrogen Oxides 1304
Recovery of Waste Sulfuric Acid 1306

Preparing Mixtures of Oleum and Sulfuric Acid........... 1310
The properties of Pure Sulfuric Acid (Monohydrate).. 1311
Transportation of Sulfuric Acid 1312
Properties of Sulfuric Acid.... 1313
Action of Sulfuric Acid on Metals.................. 1319
Action of Sulfuric Acid on Iron and Steel.................. 1319
Action of Sulfuric Acid on Lead 1322
Action of Sulfuric Acid on Platinum.................. 1324
The Analysis of Sulfuric Acid.. 1325
Gravimetric Estimation of Sulfuric Acid................. 1325
The Volumetric Estimation of Sulfuric Acid............... 1327
The Analysis of Oleum........ 1329
Detection and Estimation of Sulfur Dioxide and Sulfites.. 1332
Detection of Impurities in Sulfuric Acid................. 1334
Impurities in Commercial Sulfuric Acid................. 1336
Estimation of Acidity in Flue and Exit Gases............. 1337
De-arsenication of Sulfuric Acid 1338
Separation of Arsenic as Trichloride.................. 1340
Removal of Arsenic as Sulfide.. 1342
Chemically Pure Sulfuric Acid. 1345
Purification from Nitrogen Oxides.................... 1347
Decolorizing Sulfuric Acid..... 1348
Special Methods of Purification 1348
General Methods of Concentration.................... 1350
Theory of the Concentration of Sulfuric Acid............... 1352
Concentration in Iron Vessels.. 1353
Concentration in Lead Pans... 1358
Concentration in Glass Vessels 1360
Concentration in Silica........ 1361
Porcelain or Enamel Apparatus 1363
Concentration in Platinum Apparatus................. 1364
Concentration in Cascades.... 1367
The Gaillard Tower........... 1372
Gaillard Towers at Gretna Plant..................... 1376
Concentration by Electricity... 1380
Concentration in Vacuum Pans 1380
The Manufacture of Monohydrate..................... 1382
Concentration in a Current of Gas...................... 1382
Other Methods of Concentration..................... 1390
Electrostatic Precipitation..... 1392
The Gilchrist Concentrator.... 1396
Recent Advancement........ 1399

CHAPTER VII.

MIXED ACIDS.

Properties of Mixtures of Nitric and Sulfuric Acids........... 1403
Fortification and Acid Recovery...................... 1412
Clarifying Spent Acid......... 1412
Recovery and Fortification of Spent Acid................ 1414
Nitrocotton Spent Acid Recovery. Gretna Practice....... 1430
Denitration of Waste Acids.... 1440
Evers Denitration Process..... 1447
The V. Vender Denitration System.................... 1460
Guttmann Nitric Acid Denitrating System............. 1462
Recovery of Nitrous Fumes as Nitric Acid................ 1466
Nitric Acid Recovery by Solvents.................... 1467
Acid Valves................. 1468
Manufacture of Nitrocotton Mixed Acid, English Practice 1474
Nitration and Nitrous Fume Poisoning................. 1485
Calculation of Acid Baths..... 1485
Acid Calculation by Method of Clement and Riviere........ 1489
The Redpath Method of Acid Calculation............... 1490
The R. Fowler Method of Spent Acid Graph Construction... 1499
The Craven Method of Acid Calculation................ 1504
Analysis of Mixed and Spent Acids.................... 1504
Analysis of Mixed Nitrating Acids (English Practice).... 1511

CHAPTER VIII.

ACID TABLES.

Acid Tables.......... 1519 to 1565

CHAPTER IX.

NITROCELLULOSE THEORY.

Historical.................... 1567
The Xyloidine of Braconnot... 1567
Nitramidine of Dumas........ 1571
Schönbein and Guncotton..... 1574
Guncotton Investigations 1848–1850.................... 1586
Guncotton Development 1851–1860.................... 1588

Stability of Guncotton, and Baron von Lenk 1593
F. Abel and the Pulping of Guncotton 1599
Nitrocellulose Development, Period 1865–1870 1616
Cellulose Nitrate Advancement, Period 1871–1880 1620
Fluxation of the Art, Period 1881–1890 1630
Cellulose Nitrate Research, Period 1891–1900 1638
Chemistry of the Cellulose Nitrates 1640
The Cellulose Nitrates of Eder. 1646
Researches of Vieille 1650
Investigations of Lunge 1656
Chemistry of the Cellulose Nitrates. Investigations 1901–1910 1667
Developments in Chemistry of Cellulose Nitrates, 1911–1920 1677
Theory of Nitration 1682
Nomenclature of the Cellulose Nitrates 1690
Pharmacopeial Nitrocelluloses. 1694
Properties of the Cellulose Nitrates 1697
Stability of the Cellulose Nitrates 1700
Nitrocellulose Solubility 1720
Viscosity of Nitrocellulose 1729
Hygroscopicity of Cellulose Nitrates 1750
Density of Nitrocellulose 1755
Optical Properties 1757
Electrical Properties 1766
Physical Properties of Collodion Membranes 1768
Reduction of Inflammability 1776
Ballistics of Nitrocellulose 1793
The Action of Fungi on Nitrocellulose 1802
Straw Nitrocellulose 1803
Nitrated Corn Pith 1805
Nitrojute 1807
Nitrolignin 1808
Nitrated Paper 1815
Nitrated Starch 1816
Nitrates of the Carbohydrates. 1843
Nitrosaccharose 1849
Nitrodextrin (Nitrodextrose) 1853
Nitroglucose 1854
Nitrated Molasses 1855
Nitrolactose 1856
Nitroerythrite 1857
Nitromannite 1862
Nitrated Resins 1869
Other Nitrated Celluloses 1871
Pyroxylins of Low Nitrogen Content 1882
Recovery of Nitrocellulose 1884
Uses of Nitrocellulose in the Dry State 1886
Preparations of Acid-Proof Nitrated Filtercloth 1890
Dyeing Nitrocellulose 1893
Amorphous Nitrocellulose 1895
Indurating Nitrocellulose 1897
Denitration of Nitrocellulose 1898
Nitrates of Hydrocellulose and Oxycellulose 1900
Xyloidins 1903
Cellulose Nitrites 1905
Cellulose Sulfuric Esters 1907
Nitrated and Chlorated Guncotton 1911
Layout and Construction of Modern Guncotton Plant 1912
Dangers in Connection with the Nitration of Cellulose 1925
Transportation of Nitrocellulose 1927

CHAPTER X.

NITRATION OF CELLULOSE.

Synopsis of This Chapter 1933
Nitration of Cellulose by Hand 1934
Abel Method of Nitration 1940
Direct Dipping Method of Cellulose Nitration 1943
The Centrifuge in Cellulose Nitration 1952
Centrifugal Nitration of Cellulose 1955
Selwig & Lange Nitrating Centrifugals 1956
Wolfshohl Automatic Cotton Steeper 1964
Tolhurst Nitrating Centrifugal 1968
Vacuum Cellulose Nitration 1970
Other Centrifugal Nitration Processes 1973
The Thomson Displacement Process 1978
The Dupont Mechanical System of Cotton Nitration 1994
Other Nitration Methods 2003
Nitration of Cotton for Cheaper Grades of Pyroxylin 2032
Nitration of Paper 2033
V. Tribouillet and L. de Besauncele Process for Paper Nitration 2037
Hyatt's Paper Nitration Process 2038
The Swan Apparatus for Paper Nitration 2046

Other Methods of Paper Nitration.... 2047
Manufacture of Nitrolignin.... 2050
Efficiency of Various Nitration Methods.... 2054
Preliminary Washing of Nitrated Cellulose.... 2059
Utilization of Wash Water.... 2067
Bleaching Nitrocellulose.... 2069
Preliminary Boiling of the Nitrocellulose.... 2071
Pulping the Nitrocellulose.... 2083
Settling the Pulped Nitrocellulose.... 2095
Poaching the Nitrocellulose.... 2098
Removal of Foreign Matter.... 2102
Blending.... 2107
Screening the Pulped Nitrocellulose.... 2112
Dehydration of the Nitrocellulose.... 2114
Centrifugal Dehydration.... 2117
Centrifugal Solvent Dehydration.... 2124
Hydraulic Dehydration.... 2127
Solvent Hydraulic Dehydration 2139
Solvent Displacement without Pressure.... 2140
Drying Nitrocellulose.... 2145
Determining the Yield.... 2159
Compressed Guncotton.... 2160
Nitration of Cellulose in Great Britain.... 2188
Nitration of Cellulose at Gretna 2188
Wet Nitrocellulose Magazines. 2229
Granulation of Nitrocellulose.. 2246
Colloiding Nitrocellulose.... 2249
Co-nitration.... 2254
Classes of Cellulose Nitrates Produced in the United States 2256
Specifications for Guncotton for the United States Navy.. 2258
United States Specifications for Nitrocellulose or Pyroxylin.. 2264
British Specifications for Guncotton.... 2265
French Guncotton and Smokeless Powder Requirements... 2267
British Admiralty Specifications A-121 for Guncotton Slabs for Mines.... 2268
Prussian Regulations Regarding Moist Nitrocellulose.... 2271

CHAPTER XI.

ANALYTICAL DETERMINATIONS OF THE CELLULOSE NITRATES.

Detection of the Cellulose Nitrates.... 2273
Determination of Moisture.... 2274
Determination of Viscosity.... 2275
Viscosity by Ostwald Viscosimeter.... 2282
Viscosity by the "Ball Fall" Method.... 2285
Determination of Solubility.... 2287
Determination of Insoluble Nitrocellulose.... 2294
Unaltered Cellulose.... 2295
Mineral Constituents.... 2296
Acidity.... 2298
Alkalinity.... 2299
Sulfate (SO_3) in Nitrocotton... 2300
Mercuric Chloride in Nitrocellulose.... 2302
Determination of Fineness.... 2305
Determination of Density.... 2306
The Determination of Nitrogen 2308
Stability Tests.... 2321
Heat Tests.... 2324
The Guttmann Stability Test.. 2335
Fume Tests (Stability).... 2343
Will's Stability Test.... 2350
The Bergmann and Junk Test.. 2354
The Obermuller Test.... 2362
Other Stability (Heat) Tests... 2365
Other Stability Tests.... 2367
United States Ordnance Methods for Testing Nitrocellulose 2370
Guncotton Specifications in Great Britain.... 2373

CHAPTER XII.

HISTORICAL DEVELOPMENT OF THE CELLULOSE ESTERS.

Cellulose Ester Solvents.... 2382
Acetone and the Ketones.... 2395
Diacetone Alcohol.... 2401
Methyl Alcohol.... 2402
Ethyl Alcohol.... 2412
Propyl Alcohol.... 2428
Butyl Alcohol.... 2437
Amyl Alcohol.... 2446
Fusel Oil.... 2469
Amyl Acetate.... 2486
Other Alkyl Esters.... 2496
Camphor.... 2510
Natural Camphor.... 2510
Artificial Camphor.... 2517
Synthetic Camphor.... 2520
Camphor Substitutes.... 2535
Proteid Substitutes.... 2550
Ureas.... 2551
Solvent Recovery.... 2553
Handling of Solvents.... 2558
Paint and Varnish Removers.. 2562
Turpentine Substitutes.... 2568

Cellulose Nitrate Lacquers, Varnishes and Bronzing Liquids.................... 2572
Collodion Lacquers........... 2573
Celluloid Lacquers............ 2577
Amyl Acetate Pyroxylin Lacquers..................... 2580
Bronzing Liquids............. 2585
Imitation Gold Leaf.......... 2586
Mother of Pearl.............. 2588
Pyroxylin-Resin Lacquers..... 2590
Nitrocotton Electric Light Filaments.................... 2594
Nitrocotton Incandescent Gas Mantles................... 2595
Nitrocellulose in the Electrical Industries................ 2597
Solid Alcohol................ 2598
Other Applications of the Nitrocotton Lacquers........... 2599
Artificial Leather............ 2599
Pyroxylin Imitation Leathers.. 2604
Nitrocellulose Waterproofing Compositions.............. 2610
Enameled Paper............. 2615
Printing on Fabrics with Nitrocellulose.................. 2616
Pyroxylin Leather, Textile and Paper Cements............ 2617
Coating of Leather with Cellulose Esters................. 2618
Artificial Filaments........... 2621
Nitrocellulose Silks........... 2621
Artificial Filament Formation.. 2626
Cuprammonium Artificial Filaments.................... 2652
Pyroxylin Plastics, Celluloid Substitutes................ 2655
Development of Pyroxylin Plastic Industry............ 2657
Pyroxylin Plastic Manufacture. 2669
Re-working Celluloid.......... 2676
Cutting of Celluloid........... 2679
Inlaying Metal Goods with Celluloid................. 2680
Dyeing of Pyroxylin Plastics.. 2681
Forming Pyroxylin Plastic Sheets.................... 2682
Veneering Celluloid........... 2684
Embossing of Celluloid........ 2685
Extrusion of Plastic Rods and Tubes..................... 2688
Inlaying Celluloid with Pigment Colors.................... 2690
Celluloid in Electrical Industries 2699
Celluloid Studs............... 2703
Celluloid Eyelets............. 2704
Celluloid Collars, Cuffs and Shirt Bosom Fronts......... 2706
Celluloid Balls................ 2722
Celluloid in Phonography...... 2731
Celluloid in Photography...... 2748
Celluloid Substitutes.......... 2759
Phenol-Aldehyde Substitutes... 2767
Celloidin and Development of Cellulose Nitrates in Microscopy..................... 2779
Celloidin or Collodion Sacs.... 2784
Pharmaceutical Collodions..... 2786
Collodion in the Photographic Art...................... 2795
Photographic Collodions....... 2800
Precipitated Pyroxylin........ 2803
Dry Plates................ 2825
Collodion Emulsions.......... 2836
Pyroxylin................... 2839
Process of Emulsification...... 2840
Ripening the Emulsion........ 2842
Methods of Manufacture...... 2843
Collodion Emulsion Manipulation...................... 2845
Actions of Acids on Collodion Emulsions................. 2845
Keeping Properties of Collodion Emulsions.......... 2846
Preservatives, Organifiers, Densitizers................ 2846
Sensitizing Leather and Fabrics.................... 2847
Collodion Positives........... 2848
Collodio-chloride Paper....... 2851
Collodio-chloride Bromide Print Outs................. 2856
Collodio-chloride Gold Toning. 2856
Collodio-chloride Developing.. 2858
Collodion Carbon Prints....... 2863
Collodion Transparencies. Lantern Slides............ 2865
Enlarging Positives on Paper and Glass.................. 2867
Collodion Positives and Transfers...................... 2868
Orthochromatic Emulsion..... 2869
Light Filters. Color Screens.. 2874
Color Photography........... 2875
Screen Plates................ 2876
Color Cinematography........ 2880
Subtractive Films............ 2881
Cinematography............. 2884
Stripping Films.............. 2900
Halation and Solarization..... 2902
Celluloid Film Varnishes...... 2903
Pyroxylin Flash Light Powder. 2904
Collodion in Ceramics......... 2905
Photomechanical Processes.... 2907
X-Ray Screens.............. 2912
Collodion for Solar and Astronomical Work............. 2912

Collodion in Spectroscopy..... 2912
Photoxylography............. 2915
Celluloid Cements............ 2916
Celluloid Dishes and Measures. 2916
Celluloid Reliefs.............. 2917
Celluloid Focussing Screens.... 2917
Cellulose Nitrate Smokeless Powders.................... 2921
Development of Cellulose Nitrates in War-like Arts... 2922
Classification of Nitrocellulose-containing Powders......... 2942
Nitrocellulose-nitroglycerol Powders.................... 2948
Nitrocellulose in Cartridge Manufacture............... 2980
Carbohydrate Carboxylates (Cellulose Acetate)......... 2987
Manufacture of Acetated Cellulose....................... 3005
Cellulose Formate............ 3015
Cellulose Acetate Solvents and Plastifiers.................. 3022
Commercial Applications of Cellulose Acetates.......... 3041
Cellulose Xanthates.......... 3062
Viscose....................... 3062
Errata....................... 3085
Index of Patents............. 3087
Index of Names.............. 3253
Index of Subjects........ 3489–3709

LIST OF ILLUSTRATIONS.

1. Sphere Viscosimeter for Cellulose Solutions (Woolwich Method). 551
2. Cotton Purification (U. S. Scheme) 584
3. Cotton Purification (English Scheme) 585
4. Cummins Hydraulic Cotton Baling Press 587
5. Mechanical Handling of Cotton Bales (Gretna, Scotland) 589
6. Cotton Dry House 591
7. Sectional View of Cotton Picking Machine 593
8. Cotton Picker Room (H. M. Explosives Factory, Gretna, Scotland 595
9. The E. Lehmann Hard Waste Opener for Cotton and all Vegetable Fibers 596
10. Tipping Pressure Kier with Entire Top to Open 597
11. Cotton Purification Building, Ground Floor (E. I. du Pont de Nemours Co.) 599
12. Cotton Purification Building, Top Floor (E. I. du Pont de Nemours Co.) 601
13. Cotton Purification Building (E. I. du Pont de Nemours Co.) ... 603
14. Cotton Purification Building, Top Floor (E. I. du Pont de Nemours Co.) 605
15. Interior Filtration Plant Showing Tubes and Valve Control (E. I. du Pont de Nemours Co.) 607
16. Cotton Dry House (E. I. du Pont de Nemours Co.) 609
17. Sargent Drying Cotton Rinser 620
18. The Davis & Furber Mixing Picker for Cotton 621
19. Coggswell Mill 622
20. Scotch Picker with Condenser Roll and Apron Screens Drawn Out from Under Cylinder for Cleaning 623
21. Scotch Picker Arranged with Condenser Roll and Apron 625
22. The W. Tatham Thread Extractor for Printing Purposes 626
23. The Garnett Preparer or Knot Breaker 628
24. Hetherington Improved Willowing Machine 629
25. Cotton Dry House, Showing Delivery Aprons at End of Dryers (E. I. du Pont de Nemours Co.) 631
26. The "Proctor" Dryer for Cotton—Single Conveyor Type 633
27. "Proctor" Single Conveyor Dryer Showing Feed 635
28. Single Conveyor Dryer Viewed from Delivery End 637
29. Looking at the Feed End of "Proctor" Three Conveyor Type ... 639
30. Drying Cotton on "Proctor" Three Conveyor Dryer (Delivery End) 641
31. Side View of Chain Conveyor with Two Wire Screen Sections Attached 643
32. Cotton Bale Breaker Attached to Vertical Opener 645
33. Feeder Attached to Vertical Cotton Opener 647
34. Saco-Lowell Condenser 648
35. One-Beater Cotton Breaker with Feeder 649
36. Intermediate or Finisher Lapper for Cotton 651
37. Cotton Teasing (Nobel's Explosives Co.) 653
38. Hand Picking of Cotton for Nitration (Nobel's Explosives Co.) .. 654
39. Cotton Drying Machine (Nobel's Explosives Co.) 656
40. Cyclone Dust Collector (Nobel's Explosives Co.) 657
41. Cotton Disintegrator 659
42. Nitric Acid Still (Buffalo Foundry & Machine Co.) 744

43. Nitric Acid Still (Buffalo Foundry & Machine Co.)............. 745
44. Hart Nitric Acid Condensing Manifold........................ 748
45. Hart Nitric Acid Condenser.................................. 749
46. Niter Storage House (H. M. Explosives Factory, Gretna)....... 774
47. Loading Niter into Nitric Retort (H. M. Explosives Factory, Gretna)... 775
48. Nitric Acid Manufacture (H. M. Explosives Plant, Gretna)..... 777
49. Nitric Acid Manufacture (H. M. Explosives Plant, Gretna)..... 778
50. HNO_3 Manufacture (H. M. Explosives Factory, Gretna)........ 780
51. HNO_3 Manufacture (H. M. Explosives Factory, Gretna)........ 781
52. Hough Niter Cake Flaker..................................... 809
53. Uebel Process for Nitric Acid Manufacture................... 816
54. The Valentiner Vacuum Process for Nitric Acid Manufacture.... 819
55, 56. The Valentiner Nitric Acid Process...................... 820
57, 58. The Valentiner Nitric Acid Process...................... 821
59. The Valentiner Vacuum Process for Nitric Acid Manufacture.... 822
60. The Valentiner Vacuum Process for Nitric Acid Manufacture.... 823
61. The Hough Nitric Acid Plant, as Constructed by the Buffalo Foundry & Machine Co.................................. 827
62. The Hough Nitric Acid Condenser............................. 830
63. The Nash Vacuum Pump.. 831
64. The Greisheim Plant for Nitric Acid Manufacture............. 835
65. The Niedenführ Nitric Acid Plant............................ 839
66. The Skoglund Nitric Acid Condenser.......................... 840
67. The Guttmann Nitric Acid Condensing System.................. 842
68. Schönherr Furnaces, Badische System......................... 859
69. Schönherr Furnace... 860
70, 71. Synthetic Nitric Acids (Poudrerie Nationale D'Angoulême).. 865
72. Transportation of Cyanamide................................. 866
73. Autoclaves.. 866
74, 75. Synthesis of Ammonia from the Air....................... 867
76. Catalyzers for Synthetic Nitric Acid Manufacture............ 868
77. The Birkeland-Eyde Nitrogen Fixation Furnace................ 871
78. Birkeland-Eyde Nitrogen Fixation Furnace.................... 872
79. Birkeland-Eyde Furnace...................................... 878
80. Birkeland-Eyde Electric Furnace (Diagrammatic).............. 879
81. Birkeland-Eyde Furnaces (Bjukan Saltpeter Factory).......... 880
82. The Badische Synthetic Ammonia Apparatus.................... 905
83. Lunge Two-Bulb Nitrometer................................... 965
84. Lunge Gas-Volumeter... 969
85. du Pont Nitrometer.. 973
86. Jensen Nitric Acid Concentration Plant...................... 988
87. Sulfur Storage (H. M. Factory, Gretna)...................... 1065
88. Weighed Sulfur Charges to be Burned......................... 1066
89. Sulfur Burners in Operation (H. M. Factory, Gretna)......... 1067
90. The Sachsenburgher SO_2 Burner............................. 1069
91. The Clemm and Hasenbach Process of Sulfuric Anhydride Manufacture.. 1118
92. The Badische Process of H_2SO_4 Manufacture................. 1139
93. The Badische Contact Process for H_2SO_4 Manufacture........ 1140
94. The Badische Contact Furnace................................ 1143
95. The Badische Contact Furnace................................ 1144
96. The Badische Process of SO_3 Manufacture.................... 1148
97. Badische Process for Producing Sulfur Trioxide.............. 1149
98. The Tentelew Sulfuric Acid Contact Method................... 1153
99. The Tentelew Process for Sulfuric Acid Manufacture.......... 1156
100. The Meister, Lucius & Brüning Process of Contact H_2SO_4 Manufacture.. 1159

101. The Schroeder-Grillo Process of SO_3 Manufacture.............. 1165
102. The Schroeder-Grillo Process of SO_3 Manufacture.............. 1166
103. The Schroeder-Grillo Process of Sulfuric Anhydride Manufacture. 1168
104. The Schroeder-Grillo Sulfuric Anhydride Process............... 1169
105. The Lihme Process of Sulfuric Acid Manufacture............... 1193
106. Raynaud and Pierron Process of Making Sulfuric Anhydride..... 1194
107. Raynaud and Pierron Sulfuric Anhydride Process.............. 1196
108. The Stone Apparatus for H_2SO_4 Manufacture.................. 1197
109. The Herreshoff Apparatus for SO_3 Manufacture................ 1199
110. Ferguson Process of Making Sulfuric Anhydride................ 1201
111. Herreshoff Process for Making Sulfuric Acid.................. 1202
112. Molecular Composition of Mixed Acid......................... 1407
113. Cellulose Nitrate Solubility as a Function of the Acid Composition.. 1408
114. The Brockbank Apparatus for Filtering Corrosive Liquids....... 1414
115. Mowbray Apparatus for Restoring Nitrating Baths............. 1416
116. du Pont System for Removal of Acids from Nitrocellulose 1418
117. du Pont System for Removal of Acids from Nitrocellulose 1419
118. du Pont Apparatus for Condensing and Mixing Acids 1428
119. Fairbanks Scale... 1429
120. Fairbanks Scale... 1429
121. The Evers Denitrating Plant.................................. 1449
122. The Evers Denitration System................................ 1450
123. The Evers Denitrating System................................ 1451
124. The Evers Denitrating System................................ 1452
125. The Evers Denitrating System................................ 1453
126. The Evers Denitration System................................ 1454
127. Guttmann Denitrating Stones................................. 1463
128. Guttmann System.. 1464
129. The Jahn Nitration Process................................... 1465
130. Everlasting Valve, Acid Type................................. 1469
131. Everlasting Valve, Acid Type, Screwed........................ 1470
132. Everlasting Valve, Acid Type, Flanged........................ 1471
133. Everlasting Valve, Acid Type, Double Disc.................... 1472
134. Everlasting Valve, Acid Type, with Shield..................... 1472
135. Mixed Nitrating Acid Tanks, Showing Installation of Acid Valves 1473
136. Everlasting Valve, Acid Form, with Extension Handle.......... 1474
137. Redpath Graphic Method of Nitrating Acid Calculation......... 1492
138. Redpath Graphic Method of Nitrating Acid Calculation......... 1493
139. Fowler Method of Spent Acid Calculation...................... 1500
140. Fowler Method of Spent Acid Calculation...................... 1501
141. Fowler Method of Spent Acid Calculation...................... 1504
142. Hygroscopicity of Cellulose Nitrates.......................... 1752
143. The Mühlhäuser Nitrostarch Manufacturing Method........... 1821
144. The Mühlhäuser Process of Nitrostarch Manufacture........... 1822
145. Pot Nitration of Cellulose in France.......................... 1943
146. Dipping Cotton.. 1944
147. Steeping the Cotton After Dipping............................ 1945
148. The Direct Dipping of Cellulose.............................. 1947
149. Nobel's Explosives Co.'s Tank Method of Nitration............ 1949
150. The Assadas Method of Cellulose Nitration.................... 1951
151. Selwig & Lange Nitrating Centrifugal......................... 1957
152. Selwig & Lange Nitrating Centrifugal......................... 1958
153. Selwig & Lange Centrifugal with Acid Circulation.............. 1959
154. Selwig & Lange Nitrating Centrifugal (Top View).............. 1960
155. Selwig & Lange Centrifugal with Fume Conveyor.............. 1964
156. Selwig & Lange Nitrating Equipment in France................ 1965
157. Selwig & Lange Nitrating Installation in France................ 1965

158. Wolfshohl Automatic Cotton Steeper.......................... 1966
159. Wolfshohl Automatic Cotton Steeping Appliance................ 1987
160. Tolhurst Nitrating Centrifugal................................ 1969
161. Tolhurst Acid Wringer... 1970
162. Tolhurst Finishing Centrifugal................................ 1971
163. Dumons Vacuum Nitrating Apparatus............................ 1972
164. Kron Nitrating Centrifugal.................................... 1975
165. Thomson Displacement Cotton Nitrating Apparatus.............. 1981
166. Thomson Displacement Apparatus (Sectional Elevation)......... 1981
167. Thomson Displacement Nitration............................... 1982
168. Thomson Displacement Nitrating Pan........................... 1982
169. Unit of Four Thomson Displacement Pans....................... 1983
170. Thomson Displacement Process at Picatinny.................... 1985
171. Thomson Displacement Nitration in France..................... 1986
172. Plumbing Installation for Displacement Plant................. 1986
173. View Showing Arrangement of Units in Rows.................... 1987
174. Thomson Displacememt Nitration Pans.......................... 1989
175. Cocking Method of Cotton Nitration........................... 1992
176. Arnott Acid Distributing System.............................. 1993
177. Acid Mixing and Weighing Tanks............................... 1996
178. Top Floor, Nitrating House................................... 1997
179. du Pont Mechanical Cotton Nitration.......................... 1998
180. Nitrating House, Dipper Floor................................ 1999
181. du Pont Mechanical Cotton Nitration.......................... 2000
182. Matousek Nitrating Centrifugal............................... 2003
183. Diamanti Method of Cotton Nitration.......................... 2005
184. Briailles Electrolytic Nitration Method...................... 2006
185. Schniter Cotton Nitration Process............................ 2007
186. France Method of Cotton Comminution......................... 2009
187. Mackie's Process for Cotton Nitration........................ 2010
188. Maxim Process for Cotton Nitration........................... 2013
189. Maxim Cotton Nitration Process............................... 2014
190. Beck and Nenninger Guncotton Apparatus....................... 2016
191. Henchman's Nitration Process................................. 2019
192. Cotton Nitration Process, Zellstoffabrik..................... 2020
193. Chardonnet Nitrating Apparatus............................... 2023
194. Kaltenbach Nitration Process................................. 2027
195. Muller Process for Cotton Nitration.......................... 2028
196. Morane Nitrating Apparatus................................... 2029
197. Schüpphaus & White Paper Nitration Process................... 2035
198. Schüpphaus & White Paper Nitration Process................... 2035
199. Mowbray's Paper Nitrating Apparatus.......................... 2036
200. Mowbray's Paper Nitrating Apparatus.......................... 2037
201. Tribouillet & Besaucele Nitrating Apparatus.................. 2038
202. Hyatt Tissue Paper Nitrator.................................. 2041
203. Hyatt Tissue Paper Nitrator.................................. 2041
204. Hyatt Tissue Paper Nitrator (Plan View)...................... 2042
205. Hyatt Tissue Paper Nitrator (Side View)...................... 2043
206. Swan Apparatus for Paper Nitration........................... 2046
207. Swan Apparatus for Paper Nitration........................... 2047
208. Delpy Paper Nitration Apparatus.............................. 2049
209. Selwig & Lange Automatic Guncotton Conveyor.................. 2061
210. Flack Guncotton Washer....................................... 2064
211. Flack Guncotton Washer....................................... 2065
212. Percolator Boiling Tub House................................. 2073
213. Guncotton Boiling House...................................... 2075
214. Selwig & Lange Guncotton Steam Centrifugal................... 2080
215. Installation of Hollander Pulpers............................ 2085

216. Miller Patent Duplex Beating Engine........................ 2086
217. Miller Duplex Beater.. 2086
218. Pulping House Showing Corliss Engines...................... 2091
219. Stabilization of Nitrocellulose in France.................. 2096
220. Centrifugal Pump Poachers.................................. 2097
221. Poachers as Installed at Stowmarket........................ 2099
222. Centrifugal Pump Poachers and Blending Tuns................ 2101
223. Poacher House... 2103
224. Chutes for Removing Foreign Matter......................... 2105
225. Installation of Electro-Magnets............................ 2106
226 Nitrocellulose Blenders..................................... 2109
227. Nitrocellulose Blenders Showing Stirring Arrangement....... 2110
228. Miller Open Screen.. 2113
229. Packer Open Diaphragm Screen............................... 2115
230. Union-Witham Screen Plate Vat and Fasteners................ 2116
231. Witham Screen Plates.. 2117
232. Sectional View of Tolhurst Bottom Discharge Extractor...... 2119
233. Tolhurst Self-balancing Dehydrating Centrifugal............ 2120
234. Installation of Centrifugals (Bottom Discharge)............ 2121
235. Leflaive Centrifugal Wringer............................... 2123
236. Müller Centrifugal Extractor............................... 2124
237. Selwig & Lange Centrifugal Pyroxylin Dehydrator............ 2126
238. Running Pulped Nitrocellulose Through the Wet Machine....... 2129
239. Dehydrating House Showing Presses.......................... 2131
240. Block or Cheese of Nitrocotton............................. 2132
241. Breaker for Disintegrating Nitrocotton Blocks.............. 2133
242. du Pont Pressure Dehydrator................................ 2134
243. Alcohol Displacement Nitrocotton Dehydration............... 2142
244. Alcohol Dehydration—Underside of Pot....................... 2143
245. Gentieu Guncotton Dehydrator............................... 2144
246. Edson Process for Drying Nitrocellulose.................... 2149
247. Stove for Drying Nitrocotton in Loose Form................. 2152
248. Passburg Patent Drying Chamber............................. 2154
249. Passburg Safety Vacuum Drying Apparatus.................... 2155
250. du Pont Method of Nitrocellulose Drying.................... 2157
251. Hydraulic Press for Alcohol Dehydration.................... 2161
252. Hydraulic Guncotton Press (From Below)..................... 2163
253. Compression of Guncotton................................... 2165
254. Guncotton Sectional Charges................................ 2167
255. Machine for Breaking or Sieving Nitrocotton................ 2169
256. Block Breaker House Discharge.............................. 2170
257. Guncotton Block Breaker.................................... 2171
258. Stove for Drying Nitrocotton in Primer Form................ 2177
259. Installation of Moulding Presses........................... 2178
260. Hydraulic Nitrocotton Press................................ 2179
261. Press for Moulding Nitrocotton into Primer Forms........... 2180
262. Cotton and Guncotton at Different Stages of Manufacture.... 2181
263. Block of Guncotton and Press............................... 2183
264. Compression of Guncotton into Blocks....................... 2185
265. Guncotton Block.. 2187
266. Solid Block of Compressed Guncotton........................ 2189
267. Unpulped Nitrocellulose.................................... 2191
268. Nitration of Cellulose..................................... 2192
269. Thomson Method of Cotton Nitration......................... 2193
270. Boiling the Nitrated Cellulose............................. 2196
271. Nitrocellulose Beaters or Pulpers.......................... 2198
272. Introducing Nitrocotton into the Beater.................... 2199
273. Bagging the Nitrocotton.................................... 2204

274. Centrifugalizing the Nitrocotton 2205
275. Picking over the Nitrocellulose 2206
276. Loading the Nitrocotton into the Preliminary Boiling Tubs 2213
277. Quinan Nitrocotton Dryer 2221
278. Quinan Nitrocellulose Dryer 2222
279. Individual Quinan Nitrocotton Dryer 2223
280. Nitration of Cotton at Gretna 2231
281. Du Pont Process for Granulating Nitrocellulose 2248
282. Du Pont Process for Granulating Nitrocellulose 2248
283. Cochius Viscosimeter 2277
284. Speedy Viscosimeter 2279
285. Ostwald Viscosimeter 2283
286. Viscosity Determination by Ball Fall Method 2286
287. Oddo Nitrogravimeter 2312
288. Abel Heat Test Apparatus 2342
289. Brame Constant Temperature Heating Apparatus 2350
290. Will's Apparatus for Testing Nitrocellulose 2351
291. Nitrocellulose Powders—Eight Hour Test 2354
292. Bergmann & Junk Stability Test Apparatus 2356
293. Bergmann and Junk Tubes 2357
294. Housing for Bergmann & Junk Stability Apparatus 2358
295. Dr. Camille Dreyfus 2989
296. Dr. Henry Dreyfus 2990
297. Leo Rutstein 3487

LIST OF TABLES.

PAGE.

I. Composition of the Celluloses........................ 10
II. Distillation of Carbohydrates........................ 41
III. Specific Rotatory Power of Different Types of Cellulose. 50
IV. Distillation of Cellulose and Wood.................... 58
V. Absorption of Tannin by Cellulose.................... 62
VI. Absorption of Tannin by Cellulose in Acid Solution..... 62
VII. Action of Sulfuric Acid on Cotton.................... 118
VIII. Cotton.. 119
IX. Acid Decomposition of Cellulose...................... 122
X. Reducing Properties of Hydrocellulose................. 138
XI. Action Sodium Hydroxide on Hydrocellulose........... 144
XII. Copper Number of Hydrolyzed Cellulose.............. 145
XIII. Action of Ozone on Cotton and Viscose............... 153
XIV. Action of Ozone on Mercerized Cotton............... 154
XV. Products from Oxidation of Cellulose.................. 166
XVI. Cellulose to Glucose................................ 199
XVII. Cellulose to Glucose (2.7 Atms. Pressure)............. 199
XVIII. Hydrolysis of Pine Wood........................... 212
XIX. Action of Caustic Soda on Cellulose.................. 218
XX. Action of Alkali on Cellulose......................... 221
XXI. Benzoylation of Cellulose........................... 222
XXII. Mercerization of Cotton............................ 229
XXIII. Vegetable Fibrous Materials......................... 244
XXIV. Carbon and hydrogen in Jute and Cotton.............. 247
XXV. Composition of Flax, Hemp and Spruce Wood.......... 250
XXVI. Composition of Wood............................... 254
XXVII. Destructive Distillation of Lignin.................... 256
XXVIII. Wood, Analyses of.................................. 258
XXIX. Color Reactions of Lignocellulose.................... 262
XXX. Analysis of Waste Sulfite Liquor..................... 280
XXXI. Resins in Wood Pulp............................... 288
XXXII. Products of Fermentation of Cellulose................ 341
XXXIII. Temperature Increases of Starch and Water............ 434
XXXIV. Lengths and Diameters of Cotton Fibers.............. 480
XXXV. Length of Cotton Fibers............................ 504
XXXVI. Variation in Length and Diameter of Cotton Fibers..... 507
XXXVII. Length of Staple of Cotton.......................... 507
XXXVIII. Diameter of Fibers................................. 508
XXXIX. Length of Cotton Staples............................ 509
XL. Regain for Cotton at Various Temperatures and Percentages of Humidity.......................... 510
XLI. Hygroscopicity of Cottons........................... 513
XLII. Hygroscopicity of Purified Cottons................... 514
XLIII. Percentage Moisture Absorption in Cotton............. 517
XLIV. Mineral Constituents of Cotton...................... 525
XLV. Ash in Different Varieties of Cotton.................. 525
XLVI. Mineral Constituents of Cotton Fiber................ 526
XLVII. Analyses of Cotton Fiber........................... 527
XLVIII. Tensile Strength of Cotton.......................... 572
XLIX. Strength of Single Cotton Yarns..................... 528
L. Composition of Cotton Fiber........................ 531
LI. Analyses of Mercerized Egyptian Cotton.............. 532

LII. Copper Absorption of Cotton 547
LIII. Analyses of Nitrated Cotton 558
LIV. Solubility of Aluminium in Nitric Acid 951
LV. Production of Sulfur in Various Countries, 1906–1914 Inclusive 1021
LVI. Analyses of Pyrites 1047
LVII. Analyses of Pyrites 1048
LVIII. Dimensions of Mechanical Pyrites Burners 1064
LIX. Sulfur Trioxide Content of Oleum 1126
LX. Sulfur Trioxide Content of Feed Acid, 96%–100% 1126
LXI. Sulfur Trioxide Content of Oleum, 88%–96% 1126
LXII. Conversion of SO_2 and O_2 at Various Temperatures 1135
LXIII. Sulfur Dioxide and Oxygen without Nitrogen 1135
LXIV. Burner-Gas Diluted with Air 1135
LXV. Specific Heat of Sulfuric Acid 1318
LXVI. Percentage of Arsenic Compounds in Sulfuric Acid 1338
LXVII. Cascade Plant and Condensers 1371
LXVIII. Electric Conductivity of Sulfuric Acid 1405
LXIX. Vapor pressure of Mixed Sulfuric-nitric Acid 1405
LXX. Approximate Weights of Mixed Acid 1513
LXXI. Reduction of Gas. Volumes 0° and 760 mm 1520
LXXII. Corrections of Barometer Readings for Temperature 1521
LXXIII. Density of Water at 0° to 36° 1521
LXXIV. Density of Water at 30° to 102° 1522
LXXV. Density of Water at 100° to 320° 1522
LXXVI. Volume in Cubic Centimeters of One Gram of Water at 0° to 36° C 1522
LXXVII. Volume in Cubic Centimeters of One Gram of Water at 30° to 102° C 1523
LXXVIII. Volume in Cubic Centimeters of One Gram of Water at 100° to 320° C 1523
LXXIX. Specific Gravity of Sodium Nitrate Solutions at 20.2° C. 1523
LXXX. Solubility of Sodium Nitrate in 100 Parts Water at t° C. 1524
LXXXI. Solubility of Sulfur Dioxide in Water 1524
LXXXII. Solubility of Sulfur Dioxide in Water 1524
LXXXIII. Equivalent of Degrees Baumé and Specific Gravity at 60° F 1525
LXXXIV. Specific Gravity of Fuming Sulfuric acid at 35° C 1527
LXXXV. Fuming Sulfuric Acid 1528
LXXXVI. Fuming Sulfuric Acid 1529
LXXXVII. Sulfuric Acid 1530
LXXXVIII. Sulfuric Acid 1532
LXXXIX. Sulfuric Acid 1535
XC. Temperature Corrections in Sulfuric Acid Gravities 1536
XCI. Influence of Temperature on the Sp. gr. of Sulfuric Acid 1537
XCII. Temperature Correction Table for Sulfuric Acid 1538
XCIII. The Thermal Properties of Sulfuric Acid and Water Mixtures 1539
XCIV. Sulfuric Acid and Water Mixtures 1540
XCV. Corrections for Hydrometer Readings 1541
XCVI. Centigrade Fahrenheit Conversion Tables 1542
XCVII. Specific Gravity Tables for Nitric Acid 1544
XCVIII. Correction of Specific Gravity of Nitric Acid Containing Nitrous Fumes 1545
XCIX. Densities of Concentrated Nitric Acid at Different Temperatures 1546
C. Nitric Acid 1548
CI. Weight of 1 cc. of Moist Nitrogen in Milligrams 1549

CII. Reducing Nitric Acid to Standard Temperature and Pressure 1550
CIII. Percentages of Nitrogen in Substances Taken 1557
CIV. Composition of Gas from Combustion of Guncotton 1627
CV. Cellulose Nitrates of Vieille 1652
CVI. Nitration Experiments of Vieille 1654
CVII. Nitration Experiments of Vieille 1655
CVIII. Effect of Washing on Guncotton 1657
CIX. Effect of Pulping on Guncotton 1657
CX. Effect of Washing on Viscosity of Guncotton 1657
CXI. Influence of Water on Nitration of Cotton 1659
CXII. Nitration of Cellulose Derivatives 1663
CXIII. Nitration Experiments of Bonge 1667
CXIV. Action Concentrated Nitric and Sulfuric Acids on Cotton 1672
CXV. Saponification of Nitrocellulose by Caustic Soda 1676
CXVI. Saponification of Nitrocellulose by Ammonium Sulfide... 1676
CXVII. Heat Test of Nitrocellulose Combinations 1704
CXVIII. Loss of Nitrogen in Heating Nitrocellulose 1707
CXIX. Solubility of Nitrocellulose 1725
CXX. Solubility of Nitrocellulose 1726
CXXI. Viscosity of Nitrocellulose Solutions 1737
CXXIII. Viscosity of Nitrocellulose in Ether-Alcohol 1744
CXXIV. Alteration of Viscosity with Time 1745
CXXV. Nitrocellulose Viscosity in Ether-Alcohol 1745
CXXVI. Viscosity/Concentration of Nitrocellulose 1746
CXXVII. Viscosity of Ether-Alcohol Nitrocellulose Solutions 1746
CXXVIII. Effect of Water on Nitrocellulose Viscosity 1748
CXXIX. Viscosity Nitrocellulose in Anhydrous Acetone 1749
CXXX. Density of Nitrocellulose 1756
CXXXI. Action Ultraviolet Rays on Smokeless Powders 1764
CXXXII. Ultraviolet Ray Decomposition of Nitrocellulose 1764
CXXXIII. Permanent Gases in Explosion of Strand Guncotton 1799
CXXXIV. Permanent Gases in Explosion of Pellet Guncotton 1799
CXXXV. Gases in Detonating Guncotton 1800
CXXXVI. Gases Evolved in Firing Cordite Powder 1800
CXXXVII. Pressures in Firing Cordite Powder 1801
CXXXVIII. Solubility of Nitrated Starch 1833
CXXXIX. Viscosity of Nitrated Starch 1833
CXL. Composition of Trojan Explosive and Grenite 1841
CXLI. Colors Produced in Dyeing Nitrocellulose 1896
CXLII. Nitrates of Oxycellulose and Hydrocellulose 1902
CXLIII. Spent Acid from Thomson Nitration Process 1989
CXLIV. Temperature Rise of Spent Acid, Thomson Process 1989
CXLV. Comparison of Nitrated Processes 2059
CXLVI. Materials Required for One Ton Nitrocellulose 2059
CXLVII. Boiling Periods for Nitrocellulose 2077
CXLVIII. Boiling Periods for Nitrocellulose 2078
CXLIX. Determination of Nitrogen in Guncotton 2320
CL. Analysis of Nitrocellulose Compounds by Nitrometer... 2322
CLI. Stability Nitrocellulose for Military Powder 2348

ABBREVIATIONS.

A. A. A. S.	American Association for the Advancement of Science
Anon.	Anonyme (Anonymous)
A. O. A. C.	Association of Official Agricultural Chemists
abs.	absolute
A. C.	Alternating current
Act.	Actien
Add.	Addition Patent
alc.	alcohol ethyl
alk.	alkaline
amp.	ampere
amt.	amount
approx.	approximate
at.	atom, atomic
atm.	atmosphere(s)
atm. pr.	atmospheric pressure
as-	assymmetric
av.	average
b.	boil(s), boiling
b. pt.	boiling point
c.	asymmetric carbon atom
cal.	calorie
cc.	cubic centimeter(s)
chem.	chemical
C. I.	cast iron
com.	commercial
comp.	composition
compd.	compound
conc.	concentrat-ed, ion
cor.	corrected
C. O. V.	Concentrated oil of vitriol
c. p.	candle power
crys.	crystals, crystallized
cu.	cubic
cu. ft.	cubic foot (feet)
cu. m.	cubic meter(s)
cwt.	hundredweight
D. C.	Direct current
d-	dextro
d.	density
diam.	diameter
dcm.	decimeter
dil.	dilute
dr.	dram
fl.	fluid
Farb.	Farbenfabriken
f. pt.	freezing point
gal.	U. S. gallon, 3785 cc.
Ges.	Gesellschaft
gm.	gram(s)
gr.	grain(s)
h. p.	horse power
hr.	hour(s)
insol.	insoluble
in.	inch
k.	kilogram
kw.	kilowatt
l.	liter(s)
l.	laevo
lab.	laboratory
lb.	Avoirdupois pound(s)
Ltd.	Limited
m.	meter
m.	meta
mfr.	manufacturer
mfg.	manufacturing
mgm.	milligram
min.	minute(s)
mm.	millimeter
mol.	molecule(s)
mol. wt.	molecular weight
m. pt.	melting point
M. S.	Mild steel
nor.	normal
n. t. p.	normal temperature and pressure (0° C, 760 mm.)
o-	ortho
ord.	ordinary
oz.	Avoirdupois ounce
p-	para
pp.	precipitate
p.	pint
qt.	quart
quant.	quantitative
recryst.	recrystallized
r. p. m.	revolution per minute
sat.	saturate(d)
sc.	scruple
sec.	second(s)
soln.	solution
Soc.	Societe
sp. gr.	specific gravity
sq.	square
S. T. P.	Standard temperature (15.56° C.) and pressure (760 mm.)
sym.	symmetrical
temp.	temperature(s)
v-	vicinal
vac.	vacuum
vol.	volume(s)
wt.	weight
°	degrees Centigrade (always)
%	per cent. by weight

TABLE OF SUMMARIES TO VOLUME ONE

Chapt.	Pages	Topics	Tables	Cuts	Foot Notes	Patents	Literature Refer- ences	Names
I	388	75	32	0	1124	3624	13665	5042
II	96	19	2	0	798	896	6583	1839
III	98	27	19	1	174	143	565	211
IV	82	11	0	40	111	238	508	466
V	344	71	1	41	1199	5116	10386	4994
VI	396	141	13	25	1676	4609	9376	5911
VII	116	21	2	30	100	111	509	155
VIII	48	0	34	0	12	—	7	20
IX	366	65	33	3	1420	1175	8359	1988
X	340	54	11	138	320	577	1014	351
XI	104	27	3	14	204	6	1216	302
XII	707	88	0	2	12473	22963	28316	12461
Total	3085	599	150	294	19611	39458	80504	33740

LIST OF ABBREVIATIONS TO LITERATURE

Prepared by DR. CARL MARX

A. and N. J.	Army and Naval Journal
Aarau, Archiv der Med.	Archiv. der Medizin, Chirurgie, und Pharmazie
Aarau, Mitth.	Mittheilungen des Aargauischen Naturforschenden Gesellschaft
Abbeville, Bull. Soc. Linn.	Compte Rendu et Bulletin de la Société Linneenne du Nord de la France
Abbeville, Mem. Soc. Emul.	Memoires de la Société d'Emulation d'Abbeville
Abeille, J.	L'Abeille, Journal d'Entomologie
Abeille mem.	L'Abeille: memoires d'Entomologie
Abeille Soc.	(Publications de la Soc. Entomologie de France.) LaAbeille. Journal de Entomologie
Acad.	Memoires de l'Academie des Sciences
Acad. Caes. Leop. Nova Acta	Nova Acta physico-medica Academiae Caes. Leopoldino-Carolinae Naturae Curiosorum
Acad. Natur. Curios. Nova Acta	Nova Acta Academiae Caesareae Leopoldino-Carolinae Germanicae Naturae Curiosorum
Acireale Accad. Atti	Atti e Rendiconti dell' Accademia di Scienze, Lettere e Arti dei Zelanti e PP. dello Studio di Acireale
Acireale, Soc. Ital. Micro. Boll.	Bollettino della Societa Italiana dei Microscopisti
Acquoy, Tijdschrift	Tijdschrift voor Wis-, Natuur-, en Wertuigkunde
Acta Math.	Acta Mathematica
Actes Soc. Helvetique	Actes de la Société Helvétique des Sciences Naturelles
Adansonia	Adansonis: Recueil d'observations botaniques
Adelaide Phil. Soc. Trans.	Transactions and Proceedings and Report of the Philosophical Society of Adeliade, South Australia
Aeronaut. J.	The Aeronautical Journal
Aeronaut. Soc. Reports	Annual Reports of the Aeronautical Society of Great Britain
Aeronaute	L'Aeronaute: bulletin mensuel international de la Navigation Aerienne
Afhandl. Fysik.	Afhandlingar i Fysik, Kemi, och Mineralogi
African Assoc. Proc.	Proceedings of the African Association for promoting the Discovery of the Interior Parts of Africa
Agen, Soc. Agric. Recueil.	Recueil des Travaux de la Société d'Agriculture, Sciences, et Arts d'Agen
Agram., Program Gymnas.	Program des k. k. Akademischen Gymnasiums zu Agram
Agric. Gaz.	The Agricultural Gazette
Agric. Gaz. N. S. Wales	Agricultural Gazette of New South Wales, The
Agric. J. India	Agricultural Journal of India
Agric. Ledg.	Agricultural Ledger
Agric. Soc. J.	The Journal of the Royal Agricultural Society of England
Agric. Stud. Gaz.	Agricultural Students' Gazette. A Quarterly Journal edited by Students at the College, Cirencester
Agron. Ztg.	Agronomische Zeitung
Aix, Acad. Mem.	Recueil de Memoires de la Société des Amis des Sciences, des Lettres, de l'Agricultur, et des Arts a Aix

Albany Inst. Proc.	Proceedings of the Albany Institute
Albany Inst. Trans.	Transactions of the Albany Institute
Alger. Bull. Soc. Climat.	Bulletin de la Societe de Climatologie Algerienne
Alk.	Alkohol
Allelod. Soc. Trans.	The transaction of the Allelodidactic Society
Allg. Berg. Ztg.	Allgemeine berg- und hüttenmännische Zeitung
Allg. Bot. Zts.	Allgemeine Botanische Zeitscrift für Systematik, Floristik, Pflanzengeographie, etc.
Allg. Deut. Naturhist. Ztg.	Allgemeine Deutsche naturhistorische Zeitung
Allg. Deut. Ornith. Ges.	See J. Ornith
Allg. Fischerei Ztg.	Allgemeine Fischerei Zeitung
Allg. Forst-Jagd-Zts.	Allgemeine Forst- und Jagd-Zeitung
Allg. Gerber-Ztg.	Allgemeine Gerber-Zeitung
Allg. Schweiz. Ges. Gesam. Naturwiss.	See Zürich, Schweiz. Ges. N. Denkschr.
Allg. Syn. Suikerfab.	Algemeen Syndicat van Suikerfabrikanten in Nederl.-Indie. With Arch-Suikerind, etc.
Allg. Zts. Bierbr. Malzfabr.	Allgemeine Zeitschrift für Bierbrauerei und Maz.l fabrikation
Allier, Bull. Soc. Emul.	Bulletin de las Société d'Émulation du département de l'Allier: Sciences, Arts, et Belles-Lettres
Alpina	Alpina, eine Schrift der genauen Kenntniss der Alpen gewidmet; von Carl Ulisses von Salis und J. R. Steinmueller
Altenburg Mitth.	Mittleilungen aus dem Osterlande; herausgegeben von der Naturforschenden Gesellschaft zu Altenburg
Amat. Mechan. Soc. J.	The (Quarterly) Journal of the Amateur Mechanical Society
Amer. Acad. Mem.	Memoirs of the American Academy of Arts and Sciences
Amer. Acad. Proc.	Proceedings of the American Academy of Arts and Sciencess
Amer. Agric.	American Agriculturist
Amer. Ann. Phot.	American Annual of Photography
Amer. Apoth. Ztg.	Deutsch-Amerikanische Apotheker Zeitung
Amer. Artisan	American Artisan
Amer. Assoc. Proc.	Proceedings of the American Association for the Advancement of Science
Amer. Brewers Rev.	American Brewers Review
Amer. Builder	The American Builder
Amer. Chem. J.	American Chemical Journal
Amer. Chemist	American Chemist
Amer. Drug.	American Druggist and Pharmaceutical Record
Amer. Electrochem. Soc.	American Electrochemical Society
Amer. Engin. & Railroad J.	American Engineer (Car Builder), and Railroad Journal
Amer. Ethnol. Soc. Trans.	Transactions of the American Ethnological Society
Amer. Entom. Soc. Trans.	Transactions of the American Entomological Society and Proceedings of the Entomological Section of the Academy of Natural Sciences
Amer. Fertilizer	American Fertilizer, The
Amer. Food J.	American Food Journal
Amer. Gas Light J.	American Gas Light Journal, The
Amer. Geogr. Soc. Bull.	Bulletin of the American Geographical and Statistical Society
Amer. Geogr. Soc. J.	Journal American Geographical Society, New York
Amer. Geogr. Soc. Proc.	Proceedings of the American Geographical and Statistical Society of New York

Amer. Geol. and Nat. Assoc. Reports	Reports of the Meetings of the Association of American Geologists and Naturalists at Philadelphia
Amer. J. Conchol.	American Journal of Conchology
Amer. J. Dent. Sci.	American Journal of Dental Science
Am. J. Math.	American Journal of Mathematics
Amer. J. Med. Sci.	American Journal of the Medical Sciences.
Amer. J. Otol.	The American Journal of Otology
Amer. J. Pharm.	American Journal of Pharmacy
Amer. J. Physiol.	The American Journal of Physiology
Amer. J. Physiol., Boston	American Journal of Physiology, Boston
Amer. J. Psychol.	The American Journal of Psychology
Amer. J. Pub. Health	American Journal of Public Health
Amer. J. Sci.	The American Journal of Science
Amer. Mach.	American Machinst
Amer. Math. Soc.	See N. Y. Amer. Math. Soc.
Amer. Med.	American Medicine
Amer. Med. Assoc. Trans.	Transactions of the American Medical Association
Amer. Med. Phil. Reg.	The American Medical and Philosophical Register; or Annals of Medicine, Natural History, Agriculture, and the Arts
Amer. Med. Recorder	American Medical Recorder
Amer. Meteorol. J.	American Meteorological Journal
Amer. Micro. J.	The American Quarterly Microscopical Journal. With which is also published the Transaction of the New York Microscopical Society
Amer. Micro. Soc. Proc.	Proceedings of the American Microscopical Society
Amer. Micro. Soc. Trans.	Transactions of the American Microscopical Society
Amer. Mineral. J.	The American Mineralogical Journal
Amer. Min. Gaz.	The American Mining Gazette and Geological Magazine
Amer. Monthly Micro. J.	American Monthly Microscopical Journal
Amer. Mus. Bull.	Bulletin of the American Museum of Natural History
Amer. Mus. Mem.	Memoirs of the American Museum of Natural History
Amer. Natur.	American Naturalist
Amer. Ophthalm. Soc. Trans.	Transactions of the American Ophthalmological Society
American Perfumer	American Perfumer and Essential Oil Review, The
Amer. Phil. Soc. Proc.	Proceedings of the American Philosophical Society held at Philadelphia
Amer. Phil. Soc. Trans.	Transactions of the American Philosophical Society, held at Philadelphia, for promoting useful knowledge
Amer. Phot.	American Photography
Amer. Poly. J.	The American Polytechnic Journal
Amer. Quart. J. Agric.	American Quarterly Journal of Agriculture and Science
Amer. Reports State Entom.	See Ill., Mass., Mo., N. Y.
Amer. Soc. Agr. Sci. Proc.	Proceedings of the Society for the Promotion of Agricultural Science
Amer. Soc. Civ. Engin. Trans.	Transactions of the American Society of Civil Engineers
Amer. Soc. Micro. Proc.	Proceedings of the American Society of Microscopists
Amer. Sugar. Ind.	American Sugar Industry and Beet Sugar Gazette, The
Amer. Vet. Rev., N. Y.	American Veterinary Review, N. Y.
Amherst. Agric. Sta. Report	Annual Report of the State Agricultural Experiment Stations, at Amherst, Mass.
Amici, Giorn. Loscano	Giornale Loscano di Scienze medichi, fisiche e naturali
Amiens Acad. Sci. Mem.	Memoirs de l'Academie des Sciences, des Lettres et des Arts d'Amiens

Ammon, Monatschr. Med.	Monatschrift für Medecin, Augenheilkunde, und Chirurgie
Ammon, Zts. Opthalm.	Zeitschrift für die Ophthalmologie
Amsterdam	Werken van het Genootschap ter Bevordering der Natuur-, Geneesen Heelkunde. See Maandbl. Nat.
Amsterdam, Akad. Jaarb.	Jaarboek van de koningklijke Akademie van Wetenschappen gevestigd te Amsterdam
Amsterdam, Akad. Proc.	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings of the Section of Sciences
Amsterdam, Akad. Verh.	Verhandelingen der koninklijke Akademie van Wetenschapp.
Amsterdam, Akad. Versl. Mededeel.	Verslagen en Mededeelingen der Koninklijke Akademie van Wetenschappen. Afdeeling Naturkunde
Amsterdam, Akad. Wet. Proc.	Processen-Verbaal van de gewone Vergaderingen der Koninklijke Akademie van Wetenschappen. Afdeeling Natuurkunde.
Amsterdam, Archief Wisk. Genoots.	Archief uitgegeven door het Wiskundig Genootschap
Amsterdam Bijdr. Dierk.	Bijdragen tot de Dierkunde uitgegeven door the (Konincklijk Zoologisch) Genootschap Natura Artis Magistra, te Amsterdam
Amsterdam, Bull. Congr. Bot.	Bulletin du Congres International de Botanique et d'Horticulture reuni a Amsterdam
Amsterdam Congr. Bot. Actes	Actes du Congres International de Botanistes, d'Horticulteurs.....tenu a Amsterdam, en 1877
Amsterdam Genootsch. "Natura Artis Magistra"	See Amsterdam Bijdr. Dierk
Amsterdam Genootsch. Nat.-, Genees- en Heelkunde	See Maandbl. Nat.
Amsterdam, Het Inst.	Het Instituut
Amsterdam, Mengelwerk	Mengelwerk von uitgeleezene en andere Wisen Natuurkundige Verhandelingen
Amsterdam, Nieuw. Verh.	Nieuwe Verhandelingen der eerste Klasse van het Koninklijk Nederlandsche Instituut van Wetenschapen, en Schoone Kunsten te Amsterdam
Amsterdam, Nieuw. Wis. Voorstel.	Verzameling van nieuwe wiskundige Voorstellen door de Leden van het Wiskundig Genootschap, onder de zinspreuk: *Een onvermoeide arbeid komt alles te boven*, elkander tot onderlinge oefening opgegeven
Amsterdam Nederl. Aardr. Genootsch. Tijdschr.	Tijdschrift van het (Kon.) Nederlandsch. Aardrijkskundig Genootschap, gevestigd te Amsterdam
Amsterdam, Onderz. Phys. Lab.	Onderzoekingen gedaan in het Physiologisch Laboratorium van de Doorluchtige en Klinische Scholen te Amsterdam
Amsterdam, Tijdschr. Natuurk. Wetens.	Tijdschrift voor Natuurkundige Wetenschappen en Kunsten
Amsterdam, Tijdschr. Wis. Natuurk. Wetens.	Tijdschrift voor de Wis- en Natuurkundige Wetenschappen, Letterkunde, en Schoone Kunsten te Amsterdam
Amsterdam, Verh.	Verhandelingen der Eerste Klasse van het Koninklijk Nederlandsche Instituut van Wetenschappen, Letterkunde, en Schoone Kunsten te Amsterdam
Amsterdam, Verh. Genoots. Geneesk.	Verhandelingen van het Genootschap ter Bevordering der Geneesen Heilkunde, en Schoone Kunsten te Amsterdam
Amsterdam, Verzam. Ber. Navig.	Verzameling van Berichten over eenige onderwerpen des Navigatie

Amsterdam Zool. Genootsch. "Natura Artis Magistra"	See Nederl. Tijdschr. Dierk.
Anales agron.	Anales Agronomicos
Anales fis. quim.	Anales de la sociedad espanola de fisica y quimica
Anales inst. med. nacional	Anales del instituto medico nacional
Anales Mineria Mex.	Anales de la Mineria Mexicana, Revista de Minas
Analyst	The Analyst, including the Proceedings of the Society of Public Analysts
Anat.	Anatomie
Anat. Anz.	Anatomischer Anzeiger. Centralblatt für die Gesamte Wissenschaftliche Anatomie. (Amtliches Organ der Anatomischen Gesellschaft)
Anat. Ges.	See Anat. Anz.
Anat. Hefte	Anatomische Hefte. Referate und Beiträge (Beiträge und Referate) zur Anatomie und Entwickelungsgeschichte.
Anat. Soc. Proc.	See J. Anat. Physiol.
Anat. Studien	Anatomische Studien
Angers Acad. Sci. Mem.	Memoires de l'Academie des Sciences et Belles-Lettres d'Angers
Angers, Ann. Soc. Linn.	Annales de la Société Linneenne du departement de Maine et Loire
Angers, Mem. Soc. Agric.	Mémoires de la Société d'Agriculture, Sciences, et Arts
Angers, Soc. Sci. Bull.	Bulletin de la Société d'Etudes Scientifiques d'Angers
Ann.	Liebig's Annalen der Chemie
Ann. Bot.	Annals of Botany
Ann. Chim.	Annales de Chimie
Ann. Chim. anal.	Annales de Chimie analytique applique á l'Industrie, a l'Agriculture, á la Pharmacie et á la Biologie
Ann. chim. farm.	Annali di Chimica e de farmacologia
Ann. Chim. Phys.	Annales de Chimie et de Physique
Ann. Chimica	Annali di Chimica (Medico-Farmaceutica e di Farmacologia)
Ann. Conduct. Ponts et Chauss.	Annales des Conducteurs des Ponts et Chaussees et des Gardes-Mines
Ann. Conserv. Arts Met.	Annales du Conservatoire des Arts et Metiers
Ann. Dermatol.	Annales de Dermatologie et de Syphiligraphie
Ann. Ecole norm.	Annales scientifiques de l'Ecole Normale superieure (L. Pasteur)
Ann. Falsif.	Annales des Falsifications
Ann. Farm. Chim.	Annali di Farmacoterapia e Chimica (Biologica)
Ann. Fis. Chim.	Annali di Fisica, Chimica, etc.
Ann. Génie Civil	Annales du Génie Civil
Ann. Gén. Sci. Phys.	Annales générales des Sciences Physiques
Ann. Geogr.	Annales de Geographie
Ann. Hydrogr.	Annales Hydrographiques
Ann. Hydrogr. Mar. Met.	Annalen der Hydrographie und Maritimen Meteorologie. Organ des Hydrographischen Bureaus (Amtes) und der Deutschen Seewarte
Ann. hyg. pub.	Annales d'hygiene publique
Ann. Ind.	Annales industrielles, par Fredureau, etc.
Ann. Inst. Pastuer	Annales de l'Institut Pasteur
Ann. Landw.	Annalen der Landwirthschaft in den K. Staaten
Ann. Landw. Wochenbl.	Annalen der Landwirtschaft, Wochenblatt
Ann. Mag. Natur. Hist.	The Annals and Magazine of Natural History, including Zoology, Botany and Geology

Ann. Matemat.	Annali di Matematica pura ed applicata
Ann. Math.	Annals of Mathematics
Ann. Med.	Annali di Medicina
Ann. Med. Psychol.	Annales medico-psychologiques; Journal de l' anatomie, Physiologie, etc., du systeme nerveux
Ann. Med. Surg.	Annals of Medicine and Surgery, or Records of the occurring Improvements and Discoveries in Medicine, Surgery, and their immediately connected Arts and Sciences
Ann. Microgr.	Annales de Micrographie specialement consacrees a la Bacteriologie, aux Protophytes et aux Protozoaires
Ann. Mines	Annales des Mines...redigees et publiees sous l'Autorisation du Ministre des Travaux Publics
Ann. Museo Ind. Ital.	Annali del R. Museo Industriale Italiano
Ann. Natur. Hist.	Annals of Natural History
Ann. Oculist	Annales d'Oculistique et de Gynecologie
Ann. Pharm.	Annals of Pharmacy
Ann. Pharm. Louvain	Annales de Pharmacie, Louvain
Ann. Phil.	Annals of Philosophy
Ann. Phys.	Annalen der Physik
Ann. Phys. Chem.	Annalen der Physik und Chemie
Ann. Ponts et Chauss.	Annales des Ponts et Chaussees
Ann. R. Staz. Chim.	Annali della R. Stazione Chimico Agraria Sperimentale di Roma
Ann. Rep., U. S. Dept. Agric.	Annual Report of the United States Department of Agriculture
Ann. sci. agron.	Annales de la science agronomique francaise et étrangére
Ann. Sci. Bot. Nat.	Annales des Sciences Naturelles, Botanique
Ann. Sci. Lomb. Veneto	Annali delle Scienze del Regno Lombardo-Veneto
Ann. Sci. Nat.	Annales des Sciences Naturelles. Botanique. Zoologie et Paleontologie, comprenant l'Anatomie, la Physiologie, la Classification et l'Histoirie Naturelle des Animaux
Ann. Sci. Univ. Jassy	Annales scientifiques de l'Université de Jassy
Ann. Scott. Natur. Hist.	The Annals of Scottish Hatural History
Ann. Surg.	Annals of Surgery
Ann. Storia Natur.	Annali di Storia Naturale
Ann. Telegr.	Annales Telegraphiques
Annab.-Buchh. Ver. Naturk. Ber.	Bericht über den Annaberg-Buchholzer Verein für Naturkunde
Annab.-Buchh. Ver. Naturk. Jahr.	Jahresbericht des Annaberg-Buchholzer Vereins für Naturkunde
Annaes Sci. Natur.	Annaes de Sciencias Naturaes
Anneè Biol.	L'Anneè Biologique. Comptes Rendus annuers des Travuax de Biologie Generale
Annot. Zool. Jap.	Annotationes Zoologicae Japonenses, Auspiciis Societatis Zoologicae Tokyonensis seriatim editae
Annuaire Ancienne Normandie	Annuaire des cinq. Departements de l'Ancienne Normandie, par l'Association Normandie
Annuaire Inst. Provinces	Annuaire de l'Institut des Provinces, des Societes Savantes, et des Congres Scientifiques
Annuaire met. France	Annuaire Meteorologique de la France
Annuaire Mines Russie	Annuaire du Journal des Mines de Russie
Anthropol. (Paris)	Materiaux pour l'Histoire de l'Homme. Revue d'Anthropologie. Revue d'Ethnographie reunis.
Anthropol. Congr.	See Congr. Int. Anthrop. C. R.
Anthropol. Inst. J.	The Journal of the Anthropological Institute of Great Britain and Ireland

Anthropol. Rev.	The Anthropological Review
Anthropol. Soc. Mem.	Memoirs read before the Anthropological Society of London
Antwerpen, Verh. Genoots. Occ. qui non.	Verhandelingen van het Genootschap: "Occidit qui non servat"
Anvers, Ann. Soc. Med.	Annales de la Societe de Medecine d'Anvers
Anvers, Congr. Sci. Geogr.	Compte-Rendu du Congres des Sciences Geographiques, Cosmographiques et Commerciales
Anvers, J. Pharm.	Journal de Pharmacie, publ. par la Soc. de Pharmacie d'Anvers
Apoth. Ztg.	Apotheker Zeitung, Berlin
Apothecary	Apothecary, Boston
Appreturzeitung	Appreturzeitung
Apt, Ann. Soc. Sci.	Annales de la Societe litteraire, scientifique et artistique d'Art (Vaucluse)
Aquila	Aquila. A Magyar Ornithologiai Központ Folyoirata. Periodical of Ornithology
Arb. Kais. Gesundhts.	Arbeiten aus dem kaiserlichen Gesundheitsamte, Berlin
Arb. pharm. Inst., D. Univ. Berlin	Arbeiten aus dem pharmazeutischen Institut der Universität Berlin
Arcachon Soc. Sci. Stat. Zool. Trav.	Société Scientifique et Station Zoologique d'Arcachon
Arcetri Oss. Pubbl.	See Firenze R. Ist. Pubbl. (Arcetri Oss)
Archief Suikerind.	Archief Suikerindustrie in Nederlandsch-Indie
Archief Wisk. Genoots.	Archief uitgegeven door het Wiskundig Genootschap
Archit. and Eng.	Architect and Engineer
Archiv. Agriculturchem.	See Hermbstädt
Archiv. Anat. Micro.	Archives d'Anatomie Microscopique
Archiv. Anat. Physiol.	Archiv. für Anatomie, Physiologie und wissenschaftliche Medicin
Archiv. Anthropol.	Archiv. für Anthropologie...Organ der deutschen Gesellschaft für Anthropologie, Ethnologie und Urgeschichte
Archiv. Anthropol. Etnol.	Archivio per l'Anthropologia e la Etnologia
Archiv. Augenheilk.	Archiv. für Augenheilkunde
Archiv. Augen-. Ohrenheilk.	Archiv. für Augen- und Ohrenheilkunde
Archiv. belges méd. mil.	Archives belges de médicine militaire
Archiv. Biol.	Archives de Biologie
Archiv. Bot. Nord. France	Archives Botaniques du Nord de la France
Archiv. Chem. Mikros.	Archiv. Chemie und Mikroskopie
Archiv. Cosmol.	Archives cosmologiques. Revue des Sciences Naturelles, avec leurs applications a la Medecine, a l'Agriculture, aux Arts, et a l'Industrie
Archiv. Dent.	Archives of Dentistry: A record of Dental knowledge; medical, surgical, microscopical, chemical, and mechanical
Archiv. Elect.	Archives de l'Electricite
Archiv. Entwickl. Organ.	Archiv. für Entwicklungsmechanik der Organismen
Archiv. exper. Path. Pharm.	Archiv. für experimentelle Pathologie und Pharmakologie
Archiv. Farmacol. sper. Roma	Archivio di Farmacolagia sperimentale e Scienze affini, Roma
Archiv. fisiol.	Archivio di fisiologia
Archiv. gen. Med.	Archives generales de Medecine
Archiv. ges. Physiol.	Archiv. für die gesammte Physiologie des Menschen und der Thiere (Pflüger)
Archiv. Heilk.	Archiv der Heilkunde

Archiv. Hyg.	Archiv. für Hygiene
Archiv. Internal Med.	Archives of Internal Medicine
Archiv. intl. pharmacodyn.	Archives internationales de pharmacodynamie et de thereapie
Archiv. Ital. Biol.	Archives Italiennes de Biologie. Revues, Résumés Reproductions des Travaux Scientifiques Italiens
Archiv. Kinderheilk.	Archiv. für Kinderheilkunde
Archiv. Math. Naturvid.	Archiv. for Mathematik og Naturvidenskab
Archiv. Math. Phys.	Archiv. der Mathematik und Physik
Archiv. Med.	Archives of Medicine
Archiv. Med. comparee.	See Rayer
Archiv. med. exp.	Archives de medicine experimentale et d'anatomie pathologique
Archiv. Med. Navale	Archives de Medecine Navale (et Coloniale)
Archiv. Med. Pharm. Militair.	Archives de Medecine et de Pharmacie Militaires
Archiv. Mikro. Anat.	Archiv. für Mikroskopische Anatomie (und Entwickelungsgeschichte)
Archiv. Miss. Sci.	Archives des Missions Scientifiques et Litteraires
Archiv. Naturgesch.	Archiv. für Naturgeschichte
Archiv. Naturk. (Dorpat)	Archiv. für die Naturkunde Liv-, Ehst- und Kurlands. Herausgegeben von der Dorpater Naturforscher-Gesellschaft
Archiv. Neerland.	Archives Neerlandaises des Sciences Exactes et Naturelles publiees par la Societe Hollandaise des Sciences a Harlem
Archiv. Ohrenheilk.	Archiv. für Ohrenheilkunde
Archiv. Ophthalm.	Albrecht von Graefe's Archiv für Ophthalmologie
Archiv. Ophthalm. Otol.	Archives of Opthalmology and Otology
Archiv. Otol.	Archives of Otology
Archiv. Parasit.	Archives de Parasitologie
Archiv. path. Anat.	Archiv für pathologische Anatomie und Physiologie und für klinische Medizin (Virchow's)
Archiv. Pharm.	Archiv. der Pharmacie; Archiv des Apothekervereins im nördlichen Deutschland.
Archiv. Pharm. og Chemi	Archiv. de Pharmaci og Chemi, Copenhagen
Archiv. Physiol.	Archives de Physiologie Normale et Pathologique
Archiv. Psychiatr.	Archiv. für Psychiatrie und Nervenkrankheiten
Archiv. Sci.	Archives of Science and Transactions of the Orleans County Society of Natural Sciences
Archiv. sci. med.	Archivio per les scienze mediche
Archiv. Sci. Phys. Nat.	Bibliotheque Universelle. Archives des Sciences Physiques et Naturelles
Archiv. Sci. Pract. Med.	Archives of Scientific and Practical Medicine
Archiv. Slaves Biol.	Archives Slaves de Biologie
Archiv. Verdauungs-krankh.	Archiv. für Verdauungs-krankheiten
Archiv. Wiss. Heilk.	Archiv. des Vereins für gemeinschaftliche Arbeiten zur Förderung der wissenschaftlichen Heilkunde
Archiv. Wiss. Prakt. Thierheilk.	Archiv. für wissenschaftliche und praktische Thierheilkunde
Archiv. Zool. Anat. Fis.	Archivio per la Zoologia, l'Anatomia, e la Fisiologia
Archiv. Zool. Exper.	Archives de Zoologie Experimentale et Generale
Arcueil, Mem. Phys.	Memoires de Physique et de Chimie de la Societe d'Arcueil
Argent. Inst. Geogr. Bol.	Boletin del Instituto Geografico Argentino
Argent. P.	Argentine Patent
Argent. Soc. Ci. An.	Anales de la Sociedad Cientifica Argentina

Arkiv. Kemi, Minerol. Geol.	Arkiv för Kemi, Mineralogi och Geologi
Arkiv. Math. Astron. Fysik	Arkiv för Mathematik Astronomi och Fysik
Armagh Nat. Hist. & Phil. Soc.	See Irish Natlist.
Arms and Expl.	Arms and Explosives
Arnhem, Natuurk.	Natuurkunde. Tijdschrift, inhoudende Phijsica, Chemie, Pharmacie, Natuurlijke Historie en Litteratuur, uitgegeven van wege het Genootschap: *Tot nut en vergenoegen*, te Arnhem
Arras, Mem. Acad.	Memoires de l'Academie d'Arras
Arras, Mem. Soc. Roy.	Memoires de la Societe Royale d'Arras
Art. J.	The Art Journal
Artiz.	The Artizan (London)
Artus, Jahr. ökon. Chemie	Jahrbuch für ökonomische Chemie, etc.
Artus, Vierteljahresschrift	Vierteljahresschrift für technische Chemie, Landwirthschaftliche Gewerbe, Fabrickwesen und Gewerbetreibende überhaupt.
Ashmol. Soc. Proc.	Abstracts of the Proceedings of the Ashmolean Society
Asiat. Researches	Asiatic Researches; or Transactions of the (Bengal) Society
Asiot. Soc. J.	Journal of the Royal Asiatic Society
Assoc. Franc. Compt. rend.	Association Francaise pour l'avancement des Sciences. Comptes Rendus
Assoc. Med. J.	See Med. Assoc. Journ.
Assur. Mag.	The Assurance Magazine (and Journal of the Institute of Actuaries)
Astron. Nachr.	Astronomische Nachrichten
Astron. Soc. Mem.	Memoirs of the Astronomical Society of London
Astron. Soc. Month. Not.	Monthly Notices of the Astronomical Society of London
Astrophys. J.	Astrophysical Journal
Atelier Phot.	Atelier des Photographen
Ateneo Ital.	L'Ateneo Italiano
Athenes Obs. Nat. Ann.	Annales de l'Observatoire National d'Athenes
Atlantis	The Atlantis, or Register of Literature and Science
Atti. Accad. Ital.	Atti dell'Accademia Italiana di Scienze
Atti. accad. Lincei	Atti della reale accademia dei Lincei, rendiconti, classe di scienze fisiche, mathematiche e naturali
Atti. Coll. Ing. Archit	Atti de Collegio degli Ingegneri ed Architetti in Milano
Atti. inst. incoragg.	Atti del R. instituto d'incoraggiamento di Napoli, Naples, Italy
Atti. R. Accad. Sci. Torino	Atti della Reale Accademia della Scienze di Torino
Atti Sci. Ital.	Riunione degli Scienziati Italiani
Atti Soc. Elvet.	Atti della Societa Elvetica delle Scienze Naturali
Aube, Mem. Soc. Agric.	Memoires de la Societe d'Agriculture, des Sciences, et des Lettres du department de l'Aube
Augsb. Naturhist. Ver. Ber.	Berichte des Naturhistorischen Vereins in Augsburg
Auk	The Auk. A Quarterly Journal of Ornithology
Ausland	Das Ausland
Aust. P.	Austrian Patent
Aust.-Hung. P.	Austro-Hungarian Patent
Australasian Assoc. Rep.	Report of the...Meeting of the Australasian Association for the Advancement of Science
Australasian J. Pharm.	Australasian Journal of Pharmacy, Melbourne
Australian Med. J.	Australian Medical Journal

Australia Med. Rec.	Medical Records of Australia
Australian P.	Australian P.
Australian Sugar J.	Australian Sugar Journal
Autun, Mem. Soc. Eduenne	Memoires de la Societe Eduenne
Auvergne, Ann. Sci.	Annales Scientifiques, Litteraires, et Industrielles de l'Auvergne
Auxerre, Bull. Soc. Sci.	Bulletin de la Societe des Sciences Historiques et Naturelles de l'Yonne
Badischen Aerzt. Verein. Mitth.	Mittheilungen des Badischen ärztlichen Vereins
Bah. P.	Bahamas Patent
Ballenstedt, Archiv.	Archiv für die neuesten Entdeckungen aus der Urwelt
Ballot, Mag. Landbouw.	Magazin voor Landbouw en Kruidkunde
Baltimore Med. Phys. Recorder	Baltimore Medical and Physical Recorder
Bamb. Naturf. Ges. Ber.	Bericht der naturforschenden Gesellschaft zu Bamberg
Barb. P.	Barbados Patent
Barcelona Acad. Bol.	Boletin de la Real Academia de Ciencias y Artes de Barcelona
Barcelona Acad. Mem.	Memorias de la Real Academia de Ciencias Naturales y Artes de Barcelona
Barrow Field Club Report	Barrow Naturalists' Field Club and Literary and Scientific Association. Annual Report and Proceedings
Basel, Ber.	Bericht über die Verhandlungen der Naturforschenden Gesellschaft in Basel
Batavia Genootsch. Verh.	Verhandlingen van het Bataviaasch Genootschap der Kunsten en Wetenschappen
Batavia, Natuur. Archief.	Natuur- en Geneeskundig Archief voor Nederlandsch-Indië
Batavia, Natuurk. Tijdschr.	Natuurkundig Tijdschrift voor Nederlandsch-Indië, uitgegeven door de Koninklijke Natuurkundige Vereeniging in Nederlandsch-Indië
Batavia, Notulen	Notulen van de Allgemeene en. Bestuurs-Vergaderingen van het Bataviaasch Genootschap van Kunsten en Wetenschappen
Batavia Obs. Obsns.	Observations made at the (Royal) Magnetical and Meteorological Observatory at Batavia
Batavia, Tijdschr.	Tijdschrift voor Indische Taal-, Land-, en Volkenkunde
Batavia, Verh. Natuurk. Vereen.	Verhandlingen der Natuurkundige Vereeniging in Nederlandsch-Indië
Bath Micro. Soc. Minutes	Extracts from the Minutes of the Bath Microscopical Society
Bath Natur. Hist. Club. Proc.	Proceedings of the Bath Natural History and Antiquarian Field Club
Bath Soc. Agric. Letters	Letters and Papers of the Bath and West of England Society for the Encouragement of Agriculture, Arts, Manufactures, and Commerce
Baugew. Ztg.	Baugewerks-Zeitung
Baumgartner Zts.	Zeitschrift für Physik, Mathematik, und verwandte Wissenschaften
Bayer. Gewerbeztg.	Bayerische Gewerbezeitung
Bayer. Kunst. Gewerbebl.	Kunst und Gewerbeblatt (Poletechn. Verein Königreich Bayern)
Bayer, Landw. Ver. Erg.	Ergebnisse landwirthschaftlicher und agrikulturchemischer Versuche an der Station des General-Comite des Bayerischen Landwirthschaftlichen Vereines in München

Bayeux, Mem. Soc. Agric.	Memoires de la Societe d'Agriculture, Sciences, Arts, et Belles-Lettres de Bayeux
Bd. Trade J.	Board of Trade Journal
Beauvais, Soc. Acad. Mem.	Memoires de la Societe Academique d'Archeologie, Sciences et Arts du Department de l'Oise
Beitr. Anat. Physiol	See Eckhard
Beitr. Anthropol. Bayerns	Beiträge zur Anthropologie und Urgeschichte Bayerns. Organ der Münchener Gesellschaft für Anthropologie, Ethnologie und Urgeschichte
Beitr. Biol. Pflanz.	Beiträge zur Biologie der Pflanzen
Beitr. Geophys.	Beiträge zur Geophysik. Abhandlungen aus dem Geographischen Seminar der Universität Strassburg. Beiträge zur Geophysik. Zeitschrift für Physikalische Erdkunde
Beitr. Kryptog. Schweiz	Beiträge zur Kryptogamenflora der Schweiz
Beitr. Mecklenb. Aerzte	Beiträge Mecklenburgischer Aerzte zur Medicin und Chirurgie
Beitr. Morphol.	Beiträge zur Morphologie und Morphogenie. Untersuchungen aus dem Anatomischen Institut su Erlangen
Beitr. Naturk. Preussens	Beiträge zur Naturkunde Preussens. Herausgegeben von der Königlichen Physikalisch-Oekonomischen Gesellschaft zu Königsberg
Beitr. Paläont. Oesterr.-Ung.	Beiträge zur Paläontologie Oesterreich-Ungarns und des Orients
Beitr. Path. Anat.	Beiträge zur Pathologischen Anatomie und Physiologie. Beirtäge zur Pathologischen Anatomie und zur Allgemeinen Pathologie
Beitr. Physiol. Morphol.	Beiträge zur Physiologie und Morphologie Niederer Organismen.
Beitr. Russ Reich.	Beiträge zur Kenntniss des Russischen Reiches und der angrenzenden Länder Asiens
Belfast, Clin. Soc. Trans.	Transactions of the Clinical and Pathological Society of Belfast
Belfast Field Club Rep.	Annual Reports and Proceedings of the Belfast Naturalists' Field Club
Belfast Natur. Hist. Soc. Proc.	Proceedings of the Belfast Natural History and Philosophical Society
Belg. Horticole	La Belgique Horticole. Annales de Botanique et d'Horticulture
Belg. P.	Belgian Patent
Bengal Asiat. Soc. J.	Journal of the Asiatic Society of Bengal
Bengal Asiat. Soc. Proc.	Proceedings of the Asiatic Society of Bengal
Bengal Govt. Records	Selections from the Records of the Bengal Government
Bengal, Phot. Soc. J.	Journal of the Photographic Society of Bengal
Ber.	Berichte der Deutschen Chemischen Gesellschaft, Berlin
Ber. deut. bot. Ges.	Berichte der deutschen botanischen Gesellschaft
Ber. pharm. Ges.	Berichte der deutschen pharmazeutischen Gesellschaft
Ber. phys. Ges.	Berichte der deutschen physikalischen Gesellschaft
Ber. Sächs. Ges. Wiss.	Berichte über die Verhandlungen der Königl. Sächs. Gesellschaft der Wissenschaften zu Leipzig
Ber. Veter. König. Sach.	Berichte über das Veterinärwesen im Königreich Sachsen
Berg. Hüttenm. Jahr.	Berg- und hüttenmannisches Jahrbuch
Berg. Hüttenm. Ztg.	Berg- und hüttenmannische Zeitung

Bergens Mus. Aarb.	Bergens Museums Aarbog for...Afhandlinger og Aarsberetning udgivne af Bergens Museum
Berggeist	Der Berggeist
Berghaus, Ann.	Annalen der Erd-, Völker- und Staatenkunde
Berghaus, Zts. Erdk.	Zeitschrift für vergleichende Erdkunde
Berlin Afrik. Ges. Mitth.	Mittheilungen der Afrikanischen Gesellschaft in Deutschland
Berlin Akad. Abh.	Abhandlungen der k. Akademie der Wissenschaften zu Berlin
Berlin Akad. Monatsber.	Monatsberichte der k. Preussischen Akademie der Wissenschaften zu Berlin
Berlin Akad. Sitzber.	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin
Berlin Ann. Telegr.	Annalen der Telegraphie
Berlin Astron. Jahr.	Berliner Astronomisches Jahrbuch
Berlin Bot. Gartens Jahr.	Jahrbuch des Königlichen Botanischen Gartens und des Botanischen Museums zu Berlin
Berlin Bot. Gartens Notizbl.	Notizblatt des Königl. Botanischen Gartens und Museums zu Berlin
Berlin Ent. Ges.	See Ill. Wschr. Ent.
Berlin Entom. Zts.	Berliner Entomologische Zeitschrift; herausg. von dem Entomologischen Verein in Berlin
Berlin Ges. Anthrop. Verh.	See Ztschr. Ethnol.
Berlin Ges. Erdk. Verh.	Verhandlungen der Gesellschaft für Erdkunde zu Berlin
Berlin Ges. Erdk. Zts.	See Berlin Zts. Erdk.
Berlin Ges. Geburtshlf. Gynäk.	See Zts. Geburtshlf. Gynäk.
Berlin Ges. Naturf. Freunde Mag.	Magazin der Gesellschaft Naturforschender Freunde zu Berlin, für die neuesten Entdeckungen in der gesammten Naturkunde
Berlin Ges. Naturf. Freunde N. Schr.	Neue Schriften derGesellschaft Naturforschender Freunde in Berlin
Berlin Ges. Naturf. Freunde Verh.	Verhandlungen der Gesellschaft Naturforschender Freunde zu Berlin
Berlin Ges. Psychiatr.	See Arch. Psychiatr.
Berlin Gesundheitsamt Biol. Abth. Arb.	Arbeiten aus der Biologischen Abtheilung für Land- und Forstwirthschaft am Kaiserlichen Gesundheitsamte
Berlin Ind. Ztg.	Industrie Zeitung, Berlin
Berlin Jahr. Pharm.	Berlinisches Jahrbuch für die Pharmacie und für die damit verbundenen Wissenschaften
Berlin Klin. Wochenschr.	Berliner klinische Wochenschrift
Berlin Mem. Acad.	Memoires de l'Academie Royale des Sciences de Berlin
Berlin Mitth. Ges. Naturf.	Mittheilungen aus den Verhandlungen der Gesellschaft Naturforschender Freunde zu Berlin
Berlin Monatsber.	Monatsberichte der K. Preuss. Akademie der Wissenschaften zu Berlin
Berlin Monatsber. Ges. Erdk.	Monatsberichte über die Verhandlungen der Gesellschaft für Erdkunde zu Berlin
Berlin Naturf. Freunde Sitzber.	Sitzungs-Berichte der Gesellschaft Naturforschender Freunde zu Berlin
Berlin Neue Zts. Geburtsk.	Neue Zeitschrift für Geburtskunde
Berlin Physiol. Ges. Verh.	See Arch. Anat. Physiol
Berlin Physik. Reichsanst. Abh.	Wissenschaftliche Abhandlungen der Physikalisch Technischen Reichsanstalt
Berlin Verh. Med. Ges.	Verhandlungen der Berliner medicinischen Gesellschaft

Berlin Zool. Mus. Mitth.	Mittheilungen aus der Zoologischen Sammlung des Museums für Naturkunde in Berlin
Berlin Zts. Erdk.	Zeitschrift der Gesellschaft für Erdkunde zu Berlin
Berlin Mitth.	Mittheilungen der Naturforschenden Gesellschaft in Bern
Berwick, Natur. Club Hist.	History of the Berwickshire Naturalists' Club
Berz. Jahr. Chem.	Berzelius Jahresberichte der Chemie
Besancon, Mem. Soc. Emul.	Memoires et Comptes Rendus de la Societe (Libre) d'Emulation du Doubs
Besancon, Seances Publ.	Seances publiques de l'Academie des Sciences, Arts, et Belles-Lettres de Besancon
Beton Eisen	Beton und Eisen
Betterave	Betterave
Beziers Soc. Sci. Bull.	Bulletin de la Société d'Etude des Sciences Naturelles de Beziers
Bianconi, Rep. Ital.	Repertorio Italiano Per la Storia Naturale
Bibl. Anat.	Bibliographie Anatomique. Revue des Travaux en langue francaise. Anatomie. Histologie. Embryoologie. Anthropologie
Bibl. Bot.	Bibliotheca Botanica. Abhandlungen aus dem Gesammtgebiete der Botanik
Bibl. Brit.	Bibliotheque Britannique, ou Recueil extrait des Ouvrages Anglais periodiques et autres; partie des Sciences et Arts
Bibl. Ital.	Giornale dell' I. R. Istituto Lomgardo di Scienze, Lettere ed Arti, e *Biblioteca Italiana*
Bibl. Math.	Bibliotheca Mathematica. Zeitschrift für Geschichte der Mathematik. Journal d'Histoire des Mathematiques. Bibliotheca Mathematica. Zeitschrift für Geschichte der mathematischen Wissenschaften
Bibl. Univ.	Bibliotheque Universelle des Sciences, Archives des Sciences Physiques et Naturelles
Bibl. Zool.	Bibliotheca Zoologica
Bied. Zentr.	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb
Bierbrauer	Der Bierbrauer
Bijdr. tot de Dierkunde	Bijdragen tot de Dierkunde
Biochem. Bull.	Biochemical Bulletin
Biochem. J.	The Bio-Chemical Journal
Biochem. Zentr.	Biochemisches Zentralblatt, Leipzig
Biochem. Zts.	Biochemische Zeitschrift
Biol. Bull.	Biological Bulletin
Biol. Zentr.	Biologisches Zentralblatt
Biophys. Zentr.	Biophysikalisches Zentralblatt, Leipzig
Birmingham Natur. Hist. & Micro. Soc. Trans.	See Midland Natlist Trans.
Birmingham Phil. Soc. Proc.	Proceedings of the Birmingham Philosophical Society
Blankenburg, Ber.	Berichte des Naturwissenschaftlichen Vereins des Harzes zu Blankenburg
Blätter Blech-Arb.	Deutsche Blätter für Blecharbeiter
Blätter Kunstgew.	Blätter für Kunstgewerbe
Blätter Zuckerrüb.	Blätter für Zuckerrübenbau
Bleekrode, Nieuw Tijdschrift	Nieuw Tijdschrift gewijd aan alle takken van Volksvlijt, Nijverheid, Landbouw, Mijnwezen, Handel, Spoorwegen, Telegraphie en Scheepvaart
Blois, Mem. Soc. Sci.	Memoires de la Société des Sciences et des Lettres de Blois
Blois, Soc. Loir et Cher Mem.	Memoires de la Société des Sciences et Lettres de Loir et Cher

Boerhaave	Boerhaave
Böhm. Ges. Abh.	Abhandlungen der Königlich Böhmischen Gesellschaft der Wissenschaften
Böhm. Ges. Wiss. Jahr.	Jahresbericht der königl. böhm. Gesellschaft der Wissenschaften
Böhm. Monatschr. Ges. Mus.	Monatschrift des Gesellschaft des Vaterländischen Museums in Böhmen
Bol. P.	Bolivia Patent
Boll. chim. farm.	Bolletino chimico farmaceutico, Milan
Boll. estac. agr. Ciudad Juarez	Boletin de la estacion agricola experimental de Ciudad Juarez
Boll. ingen.	Boletin de ingenieros
Boll. Natur. Siena	Bollettino del Naturalista Collettore, Allevatore, Coltivatore
Bologna Accad. Sci. Mem.	Memorie della (R.) Accademi delle Scienze dell' Istituto di Bologna
Bologna, Mem. Inst. Naz. Ital.	Memorie dell'Istituto Nazionale Italiano
Bologna, Mem. Soc. Med.	Memorie della Societa Medica di Bologna
Bologna, Mem. Soc. Med. Chir.	Memorie della Societa Medico-chirurgica di Bologna
Bologna, Nov. Comment.	Novi Commentarii Academiae Scientiarum Instituti Bononiensis
Bologna, Opusc.	Opuscoli della Societa Medico-chirurgica di Bologna
Bologna, Opusc. Sci.	Opuscoli Scientifici
Bologna, Opusc. Sci. N. Coll.	Nuova collezione d'Opuscoli Scientifici
Bologna Rend.	Rendiconto delle Sessioni dell' Accademia Reale delle Scienze dell' Istituto di Bologna
Bombay, Agric. Hort. Soc. Proc.	Proceedings of the Agricultural and Horticultural Society of Western India
Bombay Govt. Records	Selections from the Records of the Bombay Government
Bombay, Med. Phys. Soc. Trans.	Transactions of the Medical and Physical Society of Bombay
Bombay Natur. Hist. Soc. J.	The Journal of the Bombay Natural History Society
Bombay, Roy. Asiat. Soc. J.	The Journal of the Bombay Branch of the Royal Asiatic Society
Bone, Acad. Hippone Bull.	Bulletin de l'Academie d'Hippone
Bonn, Corresp. Blatt Nat. Hist. Ver.	Correspondenzblatt des Naturhistorischen Vereins für Rheinland und Westphalen
Bonn, Niederrhein. Ges. Sitzber.	Sitzungsberichte der Niederrheinischen Gesellschaft für Natur- und Heilkunde zu Bonn
Bonn, Untersuch. Physiol. Lab.	Untersuchungen aus dem physiologischen Laboratorium zu Bonn
Bonn, Verh. Naturhist. Ver.	Verhandlungen des Naturhistorischen Vereins der Preussischen Rheinlande und Westphalens
Bonplandia	Bonplandia
Bordeaux, Acad. Sci. Seances Publ.	Seances publiques de l'Academie Royale des Sciences, Belles-Lettres, et Arts de Bordeaux
Bordeaux, Actes Acad. Sci.	Recueil des Actes de l'Academie des Sciences, Belles-Lettres, et Arts de Bordeaux
Bordeaux, J. Med.	Journal de Medecine de Bordeaux
Bordeaux, J. Med. Prat.	Journal de Medecine pratique, ou Recueil des Travaux de la Société de Medecine de Bordeaux
Bordeaux, Mem. Soc. Med. Chir.	Memoires et Bulletins de la Société Medico-Chirurgicale des Hopitaux et Hospices de Bordeaux
Bordeaux, Mem. Soc. Sci. Phys.	Memoires de la Société des Sciences Physiques et Naturelles de Bordeaux

Bordeaux, Soc. Linn. Actes	Actes de la Société Linneenne de Bordeaux
Bordeaux, Soc. Linn. Bull.	Bulletin d'Histoire Naturelle de la Société Linneenne Bordeaux
Bordeaux, Soc. Med. Mem.	Memoires et Bulletins de la Société de Medecine et de Chirurgie de Bordeaux
Bordeaux, Soc. Sci. P.-V.	Proces-Verbaux des Seances de la Société des Sciences Physiques et Naturelles de Bordeaux
Bornemann, Der Ingenieur	Der Ingenieur
Boston J. Phil.	The Boston Journal of Philosophy and the Arts
Boston J. Natur. Hist.	Boston Journal of Natural History
Boston Med. Surg. J.	Boston Medical and Surgical Journal
Boston, Mem. Amer. Acad.	Memoirs of the American Academy of Arts and Sciences
Boston, Mem. Natur. Hist. Soc.	Memoirs read before the Boston Society of Natural History
Boston Pap. Soc. Natur. Hist.	Occasional papers of the Boston Society of Natural History
Boston, Proc. Natur. Hist. Soc.	Proceedings of the Boston Society of Natural History
Boston Soc. Med. Sci. J.	Journal of the Boston Society of Medical Sciences
Bot. Centr.	Botanisches Centralblatt. Referirendes Organ für das Gesammtgebiet der Botanik des In- und Auslandes
Bot. Centr. Beihefte	Beihefte zum Botanischen Centralblatt
Bot. Cong. Proc.	The International Horticultural Exhibition and Botanical Congress: Report of Proceedings
Bot. Gaz.	The Botanical Gazette
Bot. Jahr. (Engler)	Botanische Jahrbücher, Engler, Leipzig
Bot. Mag., Tokyo	The Botanical Magazine, Tokyo
Bot. Notiser	Botaniska Notiser
Bot. Tidsskr.	Botanisk Tidsskrift udgivet af den Botaniske Forening i Kjobenhavn
Bot. Untersuch.	Botanische Untersuchungen aus dem Physiologischen Laboratorium der landwirthschaftlichen Lehranstalt in Berlin
Bot. Untersuch. (Brefeld's)	Untersuchungen aus dem Gesammtgebiete der Mykologie
Bot. Ver. Gesamtthüringen	See Jena Geogr. Ges. Mitth.
Botan. Ztg.	Botanische Zeitung
Bot. Zentr.	Botanisches Zentralblatt
Botaniste	Le Botaniste
Bouchardat, Archiv.	Archives de Physiologie, de Therapeutique, et d'Hygiene
Boue, J. Geol.	Journal de Geologie
Boulogne, Mem. Soc. Agric.	Memoires de la Société d'Agriculture, etc., de Boulogne-sur-Mer
Bourse cuirs Liege	Bourse aux cuirs de Liege, bulletin hebdomadaire
Brandenb. Bot. Ver. Verh.	Verhandlungen des botanischen Vereins für die Provinz Brandenburg
Brass World	Brass World and Platers Guide, The
Braunk.	Braunkohle
Braunschw. Ver. Naturwiss. Jahr.	Jahresbericht des Vereins für Naturwissenschaft zu Braunschweig
Braz. P.	Brazilian Patent
Bremen Abh.	Abhandlungen herausgegeben vom Naturwissenschaftlichen Verein zu Bremen
Brenn. Ztg.	Brennerei Zeitung
Brera, Giorn. Med. Prat.	Giornale di Medicina Pratica
Brera, Nuovi Comment.	Nuovi Commentari di Medicina

Brescia, Comment. Ateneo	Commentarj della Accademia di Scienze, Lettre, ed dell'Ateneo di Brescia
Breslau, Ann. Klin. Inst.	Annalen des Klinisch-chirurgischen Instituts auf der Universität zu Breslau
Breslau, Bot. Garten Arb.	Arbeiten aus dem Königl. Botanischen Garten zu Breslau
Breslau, Gewerbebl.	Breslauer Gewerbeblatt
Breslau, Jahr. Schles. Ver. Berg.	Jahrbuch des Schlesischen Vereins für Berg- und Hüttenwesen
Breslau, Schles. Ges. Jahr.	Jahresbericht des Akademischen Naturwissenschaftlichen Vereins zu Breslau
Breslau, Studien Physiol. Inst.	Studien des Physiologischen Instituts zu Breslau
Breslau, Zts. Klin. Med.	Zeitschrift für Klinische Medicin
Brest Soc. Acad. Bull.	Bulletin de la Société Academique de Brest
Brewers J. (Lon.)	Brewers Journal and Hop and Malt Trades Review, The (London)
Brewers J., N. Y.	Brewers Journal, New York
Brick	Brick
Brick J.	Brick, Pottery and Glass Journal
Brick and Clay Record	Brick and Clay Record
Brighton, Proc. Natur. Hist. Soc.	Reports and Abstracts of the Proceedings of the Brighton and Sussex Natural History Society
Bristol Proc. Nat. Soc.	Proceedings of the Bristol Naturalists' Society
Brit. Assoc. Rep.	Report of the Meetings of the British Association for the Advancement of Science
Brit. Clay Worker	British Clay Worker, The
Brit. Food J.	British Food Journal
Brit. For. Med. Chir. Rev.	British and foreign Medico-Chirurgical Review
Brit. Inst. Publ. Health	See J. State Med.
Brit. J. Almanac	British Journal of Photography Almanac
British J. Dent. Sci.	The British Journal of Dental Science
Brit. J. Phot.	British Journal of Photography
Brit. Med. J.	British Medical Journal
Brit. Mycol. Soc. Trans.	The British Mycological Society. Transactions
Brit. Pharm. Confer. Proc.	Proceedings of the British Pharmaceutical Conference
Brit. Pharm. Confer. Trans.	Year Book of Pharmacy, comprizing Abstracts of Papers. With the Transactions of the British Pharmaceutical Conference
Brit. Colon. Drug.	British and Colonial Druggist, London
Brit. Guiana Agr. Soc.	See Timehri
Brit. Guiana P.	British Guiana Patent
Brit. Hond. P.	British Honduras Patent
Brooklyn Entom. Soc. Bull.	Bulletin of the Brooklyn Entomological Society
Brosche, Zts.	Zeitschrift für Natur- und Heilkunde
Broussais, Ann.	Annales des la Medicine Physiologique
Brown-Sequard, J. Physiol.	Journal de la Physiologie de l'Homme et des Animaux
Brugnatelli, Giorn.	Giornale di Fisica, Chimica, e Storia Naturale
Brünn Verh.	Verhandlungen des Naturforschenden Vereines in Brünn
Brux. Acad. Bull.	Bulletins de l'Academie Royale des Sciences, etc., de Belgique
Brux. Acad. Cent. Anniv.	Centieme Anniversaire de Foundation de l'Academie Royale de Belgique
Brux. Acad. Med. Belg. Bull.	Bulletin de l'Academie Royale de Medecine Belgique
Brux. Acad. Sci. Mem.	Nouveaux memoires de l'Academie Royale, des Sciences et Belles-lettres de Bruxelles

Brux. Actes Soc. Med.	Actes de la Société Medicale de Bruxelles
Brux. Ann. Soc. Entom. Belge	Annales de la Société Entomologique Belge
Brux. Ann. Soc. Malacol.	Annales de la Société Malacologique de Belgique
Brux. Ann. Trav. Pub.	Annales des Travaux Publics de Belgique
Brux. Ann. Univ. Belg.	Annales des Universites de Belgique
Brux. Bull. Belge Phot.	Bulletin Belge de la Photographie
Brux. Bull. Soc. Bot.	Bulletins de la Société Royale de Botanique de Belgique
Brux. Congr. Bot. Act.	Actes du Congres de Botanique horticole reuni a Bruxelles
Brux. Congr. Bot. (C. R.)	Congres de Botanique et d'Horticulture de 1880 tenu a Bruxelles
Brux. J. Med.	Journal de Medecine, de Chirurgie, et de Pharmacologie
Brux. J. Soc. Centr. Agric.	Journal de la Société Centrale d'Agriculture de Belgique
Brux. Mem. Couronn.	Memoires Couronnes et Memoires des Savants Entrangers
Brux. Mus. Congo Ann.	Etat Independant du Congo. Annales du Musee du Congo, publiees par ordre du Secretaire d'Etat
Brux. Mus. Hist. Natur. Ann.	Annales du Musee Royal d'Historie Naturelle de Belgique
Brux. Mus. Hist. Natur. Bull.	Bulletin du Musee Royal d'Histoire Naturelle de Belgique
Brux. Mus. Hist. Natur. Mem.	Memoires du Musee Royal d'Histoire Naturelle de Belgique
Brux. Soc. Agric. Journ.	Journal de la Société Centrale d'Agriculture de Belgique
Brux. Soc. Belge Micro. Ann.	Annales de la Société Belge de Microscopie
Brux. Soc. Belge Micro. Bull.	Bulletin (des Seances) de la Société Belge de Microscopie
Brux. Soc. Entom. Ann.	Annales de la Société Entomologique de Belgique
Brux. Soc. Entom. Mem.	Memoires de la Société Entomologique de Belgique
Brux. Soc. Linn. Bull.	Bulletin de la Société Linneenne de Bruxelles
Brux. Soc. Sci.	See Rev. Quest. Sci.
Brux. Soc. Sci. Ann.	Annales de la Société Scientifique de Bruxelles
Bucarest. Acad. Rom. Anal.	Analele Academiei Romane
Bucarest Soc. Sci. Bul.	Buletinul Societatii de Sciinte (Fizice, Fixica, Chimia si Mineralogia) din Bucuresci-Romania. Bulletin de la Société des Sciences, Bucarest-Roumanie
Buchholz	See Annab.-Buchh. Ver. Nat. Jber.
Buda, Evkönyvei	A' Magyar Tudos Tarsasag' Evkönyvei (Year Books of the Hungarian Scientific Association)
Buda, Palyamunkak.	Termeszettudomanyi Palyamunkak
Buda, Tudomanytar.	Tudomanytar Közre- bocsatja a' Magyar Tudos Tarsasag
Buffalo Bull.	Bulletin of the Buffalo Society of Natural Sciences
Builder	The Builder
Buitenzorg Inst. Bot. Bull.	's Lands Plantentuin. Bulletin de l'Institut Botanique de Buitenzorg
Buitenzorg Jard. Bot. Ann.	Annales du Jardin Botanique de Buitenzorg
Bull. Acad. Med.	Bulletin of the Academy of Medicine
Bull. Acad. roy. Belg.	Academie royale de Belgique; Bulletin de la Classes des Sciences
Bull. Acad. Sci., Cracow.	Bulletin international de l'Academie des Sciences de Cracovie

Bull. Acad. Sci., Petrograd	Bulletin de l'Academie Imperiale des Sciences de Petrograd
Bull. Amer. Inst. Min. Eng.	Bulletin American Institute of Mining Engineers
Bull. Amer. Pharm. Assoc.	Bulletin of the American Pharmaceutical Association
Bull. assoc. chim. sucr. dist.	Bulletin de l'association des chemists de sucrerie distillerie de France
Bull. Bur. Agric.	Bulletin of the Bureau of Agricultural Intelligence and of Plant Diseases
Bull. Bur. Chem. U. S. Dept. Agric.	Bulletins, Bureau of Chemistry, U. S. Department of Agriculture
Bull. Bur. Mines	Bureau of Mines Bulletin, Department of the Interior
Bull. Bur. Standards	Bulletin of the Bureau of Standards
Bull. Col. School Mines	Bulletin of the Colorado School of Mines
Bull. Dept. Agric. Jamaica	Bulletin of the Department of Agriculture, Jamaica
Bull. Dept. Agric. Trinidad	Bulletin of Agricultural Information, Department of Agriculture, Trinidad
Bull. Geol. Inst. Univ. Upsala	Bulletin of the Geological Institute of the University of Upsala
Bull. Geol. Soc. Amer.	Bulletin of the Geological Society of America
Bull. Hyg. Lab.	Bulletins of the Hygienic Laboratory, United States Public Health and Marine Hospital Service
Bull. Imp. Inst.	Bulletin of the Imperial Institute, London
Bull. Iron Assoc.	Bulletin of the American Iron and Steel Association
Bull. Johns Hopkins Hosp.	Bulletin of Johns Hopkins Hospital
Bull. Mass. Inst. Tech.	Bulletin of the Massachusetts Institute of Technology
Bull. Med. Belge.	Bulletin Medical Belge.
Bull. Musee	Bulletin du Musee de l'industrielle de Belgique
Bull. Pharmacie	Bulletin de Pharmacie
Bull. Pharmacy	Bulletin of Pharmacy
Bull. Pharm. Sud-est	Bulletin de Pharmacie du Sud-est, Montpellier
Bull. Sci. France Belg.	Bulletin Scientifique de la France et de la Belgique
Bull. Sci. Nord	Bulletin Scientifique, Historique et Litteraire du Department du Nord et des pays voisins
Bull. Sci. pharmacolog.	Bulletin des Sciences pharmacologiques
Bull. Soc. Bot. France	Bulletin de la Société Botanique de France
Bull. Soc. Bot. Belg.	Bulletin de la Société Royale de Botanique de Belgique
Bull. Soc. Chim.	Bulletin de la Société Chimique de France
Bull. Soc. Chim. Belg.	Bulletin de la Société Chimique de Belgique
Bull. Soc. Encourag.	Bulletin de la Société d'Encouragement
Bull. Soc. franc. Mineral.	Bulletin de la Société Francaise de Mineralogie
Bull. Soc. franc. Phot.	Bulletin de la Société Francaise de Photographie
Bull. Soc. geol. France	Bulletin de la Société geologique de France
Bull. Soc. Ind. Amiens	Bulletin de la société industrielle d'Amiens 1
Bull. Soc. Ind. Marseille	Bulletin de la Société industrielle de Marseille
Bull. Soc. Ind. Minerale	Bulletin de la société de l'industrie minerale
Bull. Soc. Ind. Mulh.	Bulletin de la société industrielle de Mulhouse
Bull. Soc. Ind. Nord	Bulletin mensuel de la société industrielle du Nord
Bull. Soc. Ind. Rouen	Bulletin de la société industrielle de Rouen
Bull. Soc. internatl. elect.	Bulletin de la Société internationale des electriciens
Bull. Soc. Med. Amiens	Bulletin des Travaux de la Société Medicale d'Amiens
Bull. Soc. med. Gand	Bulletin de la Société de Medecine de Gand
Bull. Soc. Mycol.	Bulletin de la Société Mycologique de France
Bull. Soc. pharm. Bord.	Bulletin de la société pharmacie de Bordeaux
Bull. Soc. phot. Belg.	Bulletin de la Société photographique de Belgique
Bull. Soc. Romane Stiin.	Buletinul societatii Romane de Stiinte
Bull. Soc. roy. pharm.	Bulletin de la société de pharmacie de Bruxelles royale
Bull. Soc. sci. med. Rennes	Bulletin de la société scientifique et medicale de l'ouest, Rennes

Bull. Soc. vaudoise	Bulletin de la Société vaudoise des Ingenieurs et des Architects
Bull. Torrey Bot. Club	Bulletin of the Torrey Botanical Club, New York
Bull. Vulc. Ital.	Bullettino del Vulcanismo Italiano (e di Geodinamica generale)
C. A.	Chemical Abstracts
Cabanis, J. Ornithol.	Journal für Ornithologie
Cadiz, Period. Mens. Cien.	Periodico mensual de Ciencias matematicas y fisicas
Caen, Acad. Mem.	Memoires de l'Academie des Sciences, Belles Lettres, et Arts de Caen
Caen, Bull. Soc. Linn. Normandie	Bulletin de la Société Linneene de Normandie
Caen, Mem. Soc. Linn. Normandie	Memoires de la Société Linneenne de Normandie
Caen, Travaux	Precis des Travaux de la Société d'Agriculture, &c. de Caen
Calcutta, J. Natur. Hist.	The Calcutta Journal of Natural History
Calcutta, Quart. J.	Quarterly Journal of the Medico-Physical Society
Calcutta Roy. Bot. Gard. Ann.	Annals of the Royal Botanic Garden, Calcutta
Calcutta, Trans. Med. Phys. Soc.	Transactions of the Medical and Physical Society of Calcutta
Cal. Acad. Bull.	Bulletin of the California Academy of Sciences
Cal. Acad. Mem.	Memoirs of the California Academy of Sciences
Cal. Acad. Natur. Sci. Proc.	Proceedings of the Californian Academy of Natural Sciences
Cal. Acad. Pap.	Occasional Papers of the California Academy of Sciences
Cal. Min. Bur. Bull.	California State Mining Bureau. Bulletin
Cal. Min. Bur. Rep.	(California State Mining Bureau). Report of the State Mineralogist
Calvados, Mem. Soc. Linn.	Memoires de la Société Linneenne du Calvados
Cambrai, Mem. Soc. Emul.	Memoires de la Société d'Emulation de Cambrai
Cambridge Mem. Analyt. Soc.	Memoirs of the Cambridge Analytical Society
Cambridge Mus. Comp. Zool. Bull.	Proceedings of the Museum of Comparative Zoology at Harvard College, Cambridge, Mass.
Cambr. Ornith. Club Bull.	Bulletin of the Nuttall Ornithological Club. A Quarterly Journal of Ornithology
Cambridge Phil. Soc. Proc.	Proceedings of the Cambridge Philosophical Society
Cambridge Phil. Soc. Trans.	Transactions of the Cambridge Philosophical Society
Cambridge, Studies Physiol. Labor	Studies from the Physiological Laboratory in the University of Cambridge
Camera Oscura	La Camera Oscura; rivista periodica universale dei progressi della Fotografia
Can.	Canadian—Canada
Can., Bot. Soc. Ann.	Annals of the Botanical Society of Canada
Can. Chem. J.	The Canadian Chemical Journal
Can. Drug.	Canadian Druggist
Can. Eng.	Canadian Engineer, The
Can. Entom.	The Canadian Entomologist
Can. Entom. Soc. Rep.	First Annual Report on the Noxious Insects of the Province of Ontario
Can. Inst. Proc.	Proceedings of the Canadian Institute (Toronto, being a continuation of "The Canadian Journal of Science, Literature and History")
Can. Inst. Trans.	Transactions of the Canadian Institute
Can. J.	The Canadian Journal of Industry, Science, and Art

Can. Naturalist	The Canadian Naturalist and Geologist, and Porceedings of the Natural History Society of Montreal
Can. P.	Canadian Patent
Can. Pat. Off. Rec.	Canadian Patent Office Record
Can. Pharm. J.	Canadian Pharmaceutical Journal and Pharmacal Gazette
Can. Rec. Sci.	The Canadian Record of Science, including the Proceedings of the Natural History Society of Montreal, and replacing the Canadian Naturalist
Can. Roy. Soc. Proc. Trans.	Proceedings and Transactions of the Royal Society of Canada
Canestrini	See Archivio Zool.
Canestrini, Archiv.	Archivio per la Zoologia, l'Anatomia, e la Fisiologia
Cannes Soc. Mem.	Memoires de la Société des Sciences Naturelles (et Historiques), des Lettres et des Beaux-Arts de Cannes, et de l'arrondissement de Grasse
Cantu, Cronaca	Cronaca
Caout. Gutta-p.	Caoutchouc et la Gutta-percha
Caradoc Field Club Trans.	Transactions of the Caradoc and Severn Valley Field Club
Cardiff Natur. Soc. Trans.	Cardiff Naturalists' Society. Report and Transactions
Carinthia	See Kärnten
Carl, Rep. Physik.	Repertorium für Experimental-Physik., etc. (Rep. der Physik)
Carlsberg Lab.	See under Kiobenh.
Carlsruhe	See Karlsruhe
Carlsruhe, Verh. Naturwiss. Ver.	Verhandlungen des Naturwissenschaftlichen Vereins
Carloinisches Medico-Chirurgisches Institut.	See under Stockh. Physiol. Lab. Mitth.
Carus, Zool. Anzeiger	Zoologischer Anzieger
Casopis	Casopis pro Pestovani Mathematiky a Fysiky. (Journal for the Advancement of Mathematics and Physica)
Casopis Cesketho Lekarn.	Casopis Cesketho Lekarnitura
Casper Vierteljahrssch.	Vierteljahrsschrift für gerichtliche und öffentliche Medicin
Casper Wochensch.	Wochenschrift für die gesammte Heilkunde
Cassel Jahr.	Jahresbericht, dann Bericht, über die Thätigkeit des Vereins für Naturkunde in Cassel
Cassier's Mag.	Cassiers's Magazine
Castings	Castings
Catania Atti Accad. Gioen.	Atti dell'Accademia Gioenia di Scienze Naturali di Catania
Catania Boll. Accad. Gioen.	Bollettino delle Sedute della Accademia Gioenia
Cattaneo Bibl. di Farm.	Biblioteca di Farmacia, Chimica, etc.
Cattaneo Giorn. Farm.	Giornale di Farmacia
Cell. Ind.	Die Celluloid Industrie
Cellule	La cellule
Cement	Cement
Cement Age	Cement Age
Cement Eng. News	Cement and Engineering News
Cement Record	Cement Record
Centr. Agrik. Chem.	Central-Blatt für Agrikulturchemie und rationellen Wirthschafts-Betrieb. Referirendes Organ für naturwissenschaftliche Forschungen in ihrer Anwendung auf die Landwirthschaft
Centr. Allg. Path.	Centralblatt für allgemeine Pathologie

Centr. Bakt.	Centralblatt für Bacteriologie und Parasitenkunde
Centr. Med. Wiss.	Centralblatt für die medicinischen Wissenschaften
Centr. Mineral.	Centralblatt für Mineralogie, Geologie und Palaeontologie
Centr. Papierfabr.	Centralblatt für Papierfabrikation
Centr. Path.	Centralblatt für Allgemeine Pathologie und Pathologische Anatomie
Centr. Physiol.	Centralblatt für Physiologie
Centr. Text. Ind.	Centralblatt für die Textil-Industrie
Centr. Zuckerind.	Centralblatt für die Zuckerindustrie
Centrztg. Optik.	Central-Zeitung für Optik und Mechanik (Elektrotechnik und verwandte Berufszweige)
Ceramique	Ceramique, La
Cette Stat. Maritime	See Montpellier Inst. Zool. Trav.
Cey. P.	Ceylon Patent
Chamb. Comm. J.	Chamber of Commerce Journal
Chambery Mem. Acad. Savoie.	Memoires de la Societe Academique de Savoie.
Charente-Inf. Soc. Sci. Ann.	Academie de la Rochelle. Societe des Sciences Naturelles de la Charente-Inferieure. Annales
Charkoff.	See Kharkov.
Charleston Med. Journ.	Charleston Medical Journal and Review
Charleston South J. Med.	The Southern Journal of Medicine
Chem. Age	Chemical Age
Chem. Centr.	Chemisches Centralblatt (1830–1906).
Chem. Coll. Reports	Reports of the Royal College of Chemistry, and Researches conducted in the Laboratories
Chem. Drug.	Chemist and Druggist, London
Chem. Drug. Australasia	Chemist and Druggist of Australasia
Chem. Eng.	Chemical Engineer
Chem. Gaz.	Chemical Gazette, The
Chem. Ind.	Chemische Industrie
Chem. Listy	Chemicke Listy
Chem. News	Chemical News
Chem. Pharm. Centr. Blatt.	Chemisch-pharmaceutisches Central-Blatt
Chem. Rev.	The Chemical Review
Chem. Rev. Fett-Harz-Ind.	Chemische Revue über die Fett-und Harz-Industrie
Chem. Tech. Mitth.	Elsner's Chemisch-Technische Mittheilungen
Chem. Tech. Rep.	Chemisch-Technisches Repertorium (Jacobsen 1862–1901)
Chem. Tech. Neuzeit	Chemische Technologie der Neuzeit
Chem. Tech. Übers.	Chemisch-Technische Übersicht (supplement to Chem. Ztg.)
Chem. Tech. Ztg.	Chemiker-und Techniker-Zeitung
Chem. Trade J.	Chemical Trade Journal and Chemical Engineer
Chem. Weekbl.	Chemisch Weekblad
Chem. World	Chemical World, The
Chem. Zentr.	Chemisches Zentralblatt (1907–)
Chem. Ztg.	Chemiker-Zeitung
Chem. Ztg. Rep.	Repertorium der Chemiker Zeitung
Chem. Zts.	Chemische Zeitschrift
Chemist	The Chemist
Chemnitz Ber.	Bericht der Naturwissenschaftlichen Gesellschaft zu Chemnitz
Cherbourg, Mem. Soc. Acad.	Memoires de la Société Academique de Cherbourg
Cherbourg, Mem. Soc. Sci.	Memoires de la Société Imperiale des Sciences Naturelles de Cherbourg

Cherbourg Soc. Sci. Natl. Mem.	Memoires de la Société Nationale des Sciences Naturelles et Mathematiques de Cherbourg
Chester Soc. Sci. Proc.	Proceedings of the Chester Society of Natural Science (and Literature)
Chicago Acad. Sci. Bull.	Bulletin of the Chicago Academy of Sciences
Chicago Acad. Sci. Bull. Nat. Hist. Surv.	The Chicago Academy of Sciences. Bulletin...of the Natural History Survey
Chicago Acad. Sci. Trans.	Transactions of the Chicago Academy of Sciences
Chicago Entom. Soc. Mem.	Occasional Memoirs of the Chicago Entomological Society
Chicago Field Columb. Mus. Publ.	Publications of the Field Columbian Museum
Chile, Anales Univ.	Anales de la Universidad de Chile
Chile P.	Chilean Patent
Chili Soc. Sci. Act.	Actes de la Société Scientifique du Chili (Actas de la Sociedad Cientifica de Chile)
Chim. et Ind.	Chimie et Industrie
Chimiste	Chimiste, Le
Christiania, Forh.	Forhandlinger i Videnskabs-Selskabet i Christiania
Christiania, Norsk Mag.	Norsk Magazin for Laegevidenskaben
Christiania Skr. (Math.-Nat. Kl.)	Skrifter udgivne af Videnskabsselskabet i Christiania. Mathematisk-naturvidenskabelig Klasse
Christiania, Univers. Lab.	Das chemische Laboratorium der Universität Christiania
Chron. ind.	Chronique de l'industrie
Chur, Jahresber. Naturf. Gesell.	Jahresbericht der Naturforschenden Gesellschaft von Graubündten in Chur
Ciment	Ciment, Le
Cincin. Soc. Natur. Hist. Jl.	The Journal of the Cincinnati Society of Natural History
Cistula Entom.	Cistula Entomologica
Civil Eng. Inst. Trans.	Transactions of the Institution of Civil Engineers
Civil Eng. J.	The Civil Engineer and Architect's Journal, etc.
Civilingenieur	Der Civilingenieur
Clay Worker	Clay Worker, The
Clermont, Mem. Acad. Sci.	Memoires de l'Academie des Sciences, Belles Lettres, Arts de Clermont-Ferrand
Cleveland Med. J.	Cleveland Medical Journal
Clin. Soc. Trans.	Transactions of the Clinical Society of London
Coblentz, Jahr. bot. Ver.	Jahresbericht des botanischen Vereines am Mitten und Niederrheine, mit botanischen Abhandlungen
Cohn, Beitr. Biol. Pflanz.	Beiträge zur Biologie der Pflanzen
Coimbra, Inst.	O Instituto, journal scientifico et letterario
Coimbra, Soc. Broter. Bol.	Sociedade Broteriana. Boletim Anual
Col. P.	Colombian Patent
Collegium	Collegium (Scientific technical supplement to Ledermarkt)
Colliery Guardian	Colliery Guardian and Journal of the Iron and Coal Trades
Colmar Soc. Hist. Natur. Bull.	Bulletin de la Société d'Histoire Naturelle de Colmar
Colombia, Contrib.	Contribuciones de Colombia a las Ciencias i a las Artes
Colombo	See Ceylon
Colorado Sci. Soc. Proc.	Proceedings of the Colorado Scientific Society
Comment. Fauna &c. Ven. Trent.	Commentario della Fauna, Flora e Gea del Veneto e Trentino
Compt. rend.	Comptes rendus hebdomadaires des Seances de l'Academie des Sciences

Compt. rend. Assoc. Franc.	Association Francaise pour l'Avancement des Sciences. Compte Rendu de la 1^{e} (-12^{e}) Session; 1872-83
Compt. rend. minerale	Comptes rendus de la Société de l'industrie minerale
Compt. rend. Soc. biol.	Comptes rendus des seances et memoires de la Société de biologie, Paris
Compt. rend. trav. lab. Carlsberg	Comptes rendus du travaux du laboratoire de Carlsberg
Concrete	Concrete
Concrete Age	Concrete Age
Concrete Constr. Eng.	Concrete and Constructional Engineering
Concrete Eng.	Concrete Engineering (no longer published separately. Combined with Cement Age)
Conegliano Scuola Vit. Enol. Ann.	Annali della R. Scuola di Viticoltura e di Enologia in Conegliano
Conegliano Scuola Vit. Enol. N. Rassegna	Nuova Rassegna di Viticoltura de Enologia della R. Scuola di Conegliano
Conegliano Scuola Vit. Enol. Riv.	La Rivista. Periodico (quindicinale, Organo) della R. Scuola di Viticoltura e di Enologia (e del Comizio Agrario) di Conegliano
Cong. P.	Congo Free State Patent
Congr. Anthropol. Compt. Rend.	Congres international d'Anthropologie et d'Archeologie prehistoriques. Comptes Rendus
Congr. Bot. Crittog. Atti	Societa Crittogamologica Italiana. Atti del Congresso Nazionale di Botanica Crittogamica in Parma
Congr. Bot. Int. Atti	Atti del Congresso Internazionale di Genova
Congr. Int. Bot. Bull.	Bulletin du Congres International de Botanique et d'Horticulture reuni a St. Petersbourg...
Congr. Internatl. Hortic. Bull.	Bulletin du Congres International d'Horticulture a Bruxelles
Congr. Internatl. Med. Atti	Atti dell' XI. Congresso Medico Internazionale
Congr. Internatl. Med. C. R.	Comptes-Rendus du XII Congres International de Medecine
Congr. Internatl. Sci. Med. C. R.	Congres Periodique International des Sciences Medicales. Compte-Rendu
Congr. Internatl. Zool. (C. R.)	Congres International de Zoologie
Connecticut, Acad. Mem.	Memoirs of the Connecticut Academy of Arts and Sciences
Connecticut Acad. Trans.	Transactions of the Connecticut Academy of Arts and Sciences
Contrib. Biol. Veg.	Contribuzioni alla Biologia Vegetale
Copenhagen	See Kjobenhavn.
Copenhagen	See Congr. Int. Sci. Med. C. R., 1884
Copenhague, Résumé	Résumé du Bulletin de la Société Royale Danoise des Sciences
Cordoba, Acad. Bol.	Boletin de la Academia Nacional de Ciencias Exactas existente en la Universidad de Cordoba
Cordoba Acad. Ci. Act.	Actas de la Academia Nacional de Ciencias en Cordoba
Corn Trade J.	Corn Trade Journal
Cornwall, J. Roy. Inst.	Journal of the Royal Institution of Cornwall
Cornwall Poly. Soc. Rep.	Royal Cornwall Polytechnic Society, Annual Report
Cornwall, Poly. Soc. Trans.	Reports and Transactions of the Royal Geological Society of Cornwall
Corresp. Blatt. Schweiz. Aerzte	Correspondenz-Blatt für Schweizer Aerzte
Corresp. Blatt Zahn.	Correspondenzblatt für Zahnärzte
Cosmos	Cosmos: Revue Encyclopedique hebdomadaire

Costa, Corrisp. Zool.	Corrispondenza Zoologica, destinata a diffondere nel regno delle Due Sicilie tutto cio che si va discuoprendo entro e fuori Europa (e vice-versa), ris guardante la Zoologia in generale
Cotteswold Club Proc.	Proceedings of the Cotteswold Naturalists' Field Club
Cracovie Acad. Sci. Bull	Bulletin International de l'Academie des Sciences de Cracovie
Cracow	See Krakow
Crell. Ann.	Chemische Annalen für die Freunde der Naturlehre, etc.
Crichton, Russ. Sammlung.	Russische Sammlung für Naturwissenschaft und Heilkunst
Cron. med. mex.	Cronica medica mexicana, Mexico
Croydon Micro. Club Proc.	Proceedings and Transactions of the Croydon Microscopical and Natural History Club
Croydon Micro. Club Rep.	. . . Report and Abstract of Proceedings of the Croydon Microscopical (and Natural History) Club
Cuba P.	Cuban Patent
Cuba, Rep. Fis. Nat.	Repertorio fisico-naturale de la isla de Cuba
Cuir	Cuir, Le
Cumberland Assoc. Trans.	Transactions of the Cumberland and Westmorland Association for the Advancement of Literature and Science
Cuyper, Rev. Univ.	Revue Universelle des Mines, de la Metallurgie, &c.
D'Alton u. Burm. Ztg. Zool.	Zeitung für Zoologie, Zootomie, und Palaeozoologie
Dan. Biol. Stat. Rep.	Report of the Danish Biological Station to the Home Department (Board of Agriculture)
Dan. P.	Danish Patent
Danzig, Neu. Schrift.	Neueste Schriften der Naturforschenden Gesellschaft in Danzig
Danzig, Schrift.	Schriften der Naturforschenden Gesellschaft in Danzig
Darmst. Beitr. Geol.	Beiträge zur Geologie des Grossherzogthums Hessen und der angrenzenden Gegenden
Darmst. Ver. Erdk. Notiz.	Notizblatt des Vereins für Erdkunde zu Darmstadt und des Mittelrheinischen Geologischen Vereins
Davenport Acad. Proc.	Proceedings of the Davenport Academy of Natural Sciences
Dax Soc. Borda Bull.	(Bulletin de la) Société de Borda, Dax (Landes)
Delft Ecole Poly. Ann.	Annales de l'Ecole Polytechnique de Delft
Delhi, Med. J.	Quarterly Medical and Surgical Journal for the North-West Provinces
Denison Univ. Sci. Lab. Bull.	Bulletin of (the Scientific Laboratories of) Denison University
Dent. Cosmos	Dental Cosmos, Philadelphia
Dent. Digest	The Dental Digest, Chicago
Dent. Rev.	The Dental Review
Deut. Amer. Apoth. Ztg.	Deutsch-Amerikanische Apotheker Zeitung, New York
Deut. Amer. Gewerbeztg.	Illustrierte Deutsch-Amerikanische Gewerbe und Industrie-Zeitung (Newark, N. J.)
Deut. Arch. Klin. Med.	Deutsches Archiv. für Klinische Medizin
Deut. Bot. Ges. Ber.	Berichte der Deutschen Botanischen Gesellschaft
Deut. Bot. Monats.	Deutsche Botanische Monatsschrift
Deut. Buchdr. Ztg.	Deutsche Buchdruker-Zeitung
Deut. Eisenbahn Ztg.	Zeitung des Vereins Deutscher Eisenbahn-Verwaltungen
Deut. Elektro. Ges.	See Zts. Elektroch.

Deut. Entom. Zts.	Deutsche Entomologische Zeitschrift (formerly *Berliner Entomologische Zeitschrift*)
Deut. Geol. Ges. Zts.	Zeitschrift der Deutschen Geologischen Gesellschaft
Deut. Gerber Ztg.	Deutsche Gerber Zeitung
Deut. Ind. Ztg.	Deutsche Industrie Zeitung
Deut. Klinik	Deutsche Klinik
Deut. Mechan. Ztg.	Deutsche Mechaniker-Zeitung
Deut. med. Wochenschr.	Deutsche medizinische Wochenschrift
Deut. Monats.	Deutsche Monatshefte
Deut. Naturf. Ber.	Amtlicher Bericht der. . .Versammlung Deutscher Naturforscher und Aerzte
Deut. Naturf. Festschr.	Festschrift für die 59. Versammlung Deutscher Naturforscher und Aerzte
Deut. Naturf. Tagebl.	Tageblatt der. Versammlung Deutscher Naturforscher und Aerzte
Deut. Naturf. Versamml. Ber.	Bericht über die Versammlung der Deutschen Naturforscher und Aerzte
Deut. Poly. Ztg.	Allgemeine Deutsche Polytechnische Zeitung (H. Grothe)
Deut. Phys. Ges. Verh.	Verhandlungen der Deutschen Physikalischen Gesellschaft. . .
Deut. Tech. Ztg.	Deutsche Techniker Zeitung
Deut. Töpfer Ziegl. Ztg.	Deutsche Töpfer und Ziegler Zeitung
Deut. Vierteljahrschr. Oeff. Gesundh.	Deutsche Vierteljahrsschrift für Gesundheitspflege
Deut. Zool. Ges.	See Zool. Anz.
Deut. Zool. Ges. Verh.	Verhandlungen der Deutschen Zoologischen Gesellschaft
Deut. Zts. Chirurg.	Deutsche Zeitschrift für Chirurgie
Deut. Zts. Thiermed.	Deutsche Zeitschrift für Thiermedicin und vergleichende Pathologie
Deut. Zuckerind.	Deutsche Zuckerindustrie
Devon. Assoc. Trans.	Transactions of the Devonshire Association for the Advancement of Science, Literature and Art
Devon & Cornwall Hatur. Hist. Soc.	See Plymouth Inst. Trans.
Diamant Ztg.	Diamant, Glas-Industrie Zeitung
Dietet. Hyg. Gaz.	Dietetic and Hygienic Gazette, The
Dijon, Acad. Sci. Mem.	Memoires de l'Academie des Sciences, Arts et Belles-Lettres de Dijon
Dijon, J. Agric.	Journal d'Agriculture de la Cote d'Or.
Dijon, Seances Acad.	Seances publiques de l'Academie des Sciences, Arts, et Belles-Lettres de Dijon
Dinant, Soc. Natur. Bull.	Bulletin de la Société des Naturalistes Dinantais
Dingl. Poly.	Dinglers Polytechnisches Journal
Donders, Archiv	Archiv für die Holländischen Beiträge zur Natur- und Heilkunde
Dorpat, Archiv	Archiv für die Naturkunde Liv-, Esth-, und Kurlands
Dorpat, Biol. Naturk.	Biologische Naturkind.
Dorpat, Naturf. Ges.	See Arch. Nat. (Dorpat)
Dorpat, Naturwiss. Abh.	Naturwissenschaftliche Abhandlungen aus Dorpat
Dorpat Pharm. Inst. Arb.	Arbeiten des Pharmakologischen Institutes zu Dorpat
Dorpat Sitzber.	Sitzungsberichte der Naturforscher-Gesellschaft bei der Universität (Jurjew) Dorpat
Dorpat Schr.	Schriften herausgegeben von der Naturforscher Gesellschaft bei der Universität (Jurjew) Dorpat
Dorset Field Club Proc.	Proceedings of the Dorset Natural History and Antiquarian Field Club

Douai Mem. Soc. Agric.	Memoires de la Société d'Agriculture, de Sciences, et d'Arts, seant a Douai
Doubs Soc. Emul. Mem.	Memoires de la Société d'Emulation du Departement du Doubs
Dove Rep. Physik.	Repertorium der Physik. Enthaltend eine vollständige Zusammenstellung der neuern Fortschritte dieser Wissenschaft
Dresden Ausz. Protokol.	Auszüge aus den Protokollen der Gesellschaft für Natur- und Heilkunde in Dresden
Dresden Denkschr. Naturwiss. Ges. Isis.	Denkschriften der Naturwissenschaftlichen Gesellschaft Isis zu Dresden
Dresden Entom. Ver. "Iris" Corresp.-Bl.	See Iris
Dresden Isis Festschr.	Festschrift der Naturwissenschaftlichen Gesellschaft Isis in Dresden
Dresden Isis Sitzber.	Sitzungsberichte und Abhandlungen der Naturwissenschaftlichen Gesellschaft Isis in Dresden
Dresden, Jahr. Natur. Heilk.	Jahresberichte für 1858–60 v. d. Gesellschaft für Natur- und Heilkunde in Dresden
Dresden, Mitth. Poly. Schule	Mittheilungen der K. Sächs. Polytechnischen Schule
Dresden, Schr. Ges. Mineral.	Auswahl aus den Schriften der unter Werner's Mitwirkung gestifteten Gesellschaft für Mineralogie
Dresden, Sitzber. Natur. Heilk.	Sitzungsberichte der Gesellschaft für Natur- und Heilkunde
D. R. P.	German Patent (Deutsches Reichs-Patent)
Drug. Circ.	Druggist's Circular
Drug Topics	Drug Topics, New York
Dublin, Geol. Soc. J.	Journal of the Geological Society of Dublin
Dublin, Hosp. Gaz.	Dublin Hospital Gazette
Dublin J. Med. Chem. Sci.	Dublin Journal of Medical and Chemical Science
Dublin J. Med. Sci.	The Dublin Journal of Medical Science
Dublin Med. Trans.	Dublin Medical Transactions
Dublin Micro. Club	See Irish Natur.
Dublin, Natur. Hist. Soc. Proc.	Proceedings of the Natural History Society of Dublin
Dublin Natur. Field Club	See Irish Natur.
Dublin, Pathol. Soc. Proc.	Proceedings of the Pathological Society of Dublin
Dublin Quart. J.	The Dublin Quarterly Journal of Science
Dublin Quart. J. Med.	Dublin Quarterly Journal of Medical Science
Dublin, Roy. Soc. J.	Journal of the Royal Dublin Society
Dublin Soc. J., Dublin Soc. Trans.	Transactions and Journal of the Dublin Society
Dublin Soc. Sci. Proc.	The Scientific Proceedings of the Royal Dublin Society
Dublin Soc. Sci. Trans.	The Scientific Transactions of the Royal Dublin Society
Dublin, Zool. Bot. Assoc. Proc.	Proceedings of the Dublin University Zoological and Botanical Association
Dudley, Geol. Soc. Proc.	Transactions of the Dudley and Midland Geological and Scientific Society
Dumfr. Gallow. Soc. Trans.	The Transactions and Journal of Proceedings of the Dumfriesshire and Galloway Natural History and Antiquarian Society
Dunkerque, Mem. Soc. Encour.	Memoires de la Société Dunkerquoise pour l'Encouragement des Sciences, des Lettres, et des Arts
Durham Univ. Phil. Soc. Proc.	Proceedings of the University of Durham Philosophical Society

Dyer, Calico Ptr.	Dyer, Calico Printer, Bleacher, Finisher, and Textile Review
Dzondi, Aeskulap	Aeskulap
Eastbourne Natur. Hist. Soc. Papers (& Trans.)	Papers (Transactions) of the Eastbourne Natural History Society
Eastbourne Natur. Hist. Soc. Proc.	The Sixth Annual Report of the Eastbourne Natural History Society
Eastbourne Natur. Hist. Soc. Trans.	Transactions of the Eastbourne Natural History Society
Echange	l'Echange. .Organe (Mensuel) des Naturalistes de la Region Lyonnaise. . .
Eckhard, Beitr.	Beiträge zur Anatomie und Physiologie
Eclairage Elect.	l'Eclairage Electrique. Revue (hebdomadaire) d(el)'Electricite
Eclect. Med. J., Cincin.	Eclectic Medical Journal, Cincinnati
Econ. Geol.	Economic Geology
Ecu. P.	Ecuador Patent
Edinb. Bot. Soc. Proc.	Proceedings of the Botanical Society of Edinburgh for the years 1855–56
Edinb. Bot. Soc. Trans.	Transactions of the Botanical Society of Edinburgh
Edinb. Field Club Trans.	Transactions of the Edinburgh Naturalists' Field Club
Edinb., Fish. Bd. Rep.	Annual Report of the Fishery Board for Scotland .
Edinb. J. Med. Sci.	Edinburgh Journal of Medical Science
Edinb. J. Natur. Geogr. Sci.	The Edinburgh Journal of Natural and Geographical Science
Edinb. J. Sci.	The Edinburgh Journal of Science
Edinb. Med. Chir. Soc. Trans.	Transactions of the Medico-Chirurgical Society of Edinburgh
Edin. Med. J.	Edinburgh Medical Journal
Edinb. Mem. Wern. Soc.	Memoirs of the Wernerian Natural History Society
Edinb. Monthly J. Med. Sci.	Edinburgh Monthly Journal of Medical Science
Edinb. Natur. Soc. Trans.	Transactions of the Edinburgh Field Naturalists' and Microscopical Society, instituted as the Edinburgh Naturalists' Field Club
Edinb. N. Phil. J.	The Edinburgh New Philosophical Journal
Edinb. Phil. J.	The Edinburgh Philosophical Journal
Edinb. Plin. Soc. Trans.	Transactions of the Plinian Society
Edinb. Proc. Phys. Soc.	Proceedings of the Royal Physical Society of Edinburgh
Edinb. Roy. Coll. Physns. Lab. Rep.	Reports from the Laboratory of the Royal College of Physicians, Edinburgh
Edinb. Roy. Soc. Proc.	Proceedings of the Royal Society of Edinburgh
Edinb. Roy. Soc. Trans.	Transactions of the Royal Society of Edinburgh
Edinb. Trans. Scot. Soc. Arts	Transactions of the Royal Scottish Society of Arts
Eisen Ztg.	Eisen Zeitung
Ekaterinburg	See Iekaterinenb.
Elberfeld Naturwiss, Ver. Jahr.	Jahres-Bericht des Naturwissenschaftlichen Vereins in Elberfeld
Elec. Rev.	The Electrical Review
Elec. Soc. Trans.	The Transactions and Proceedings of the London Electrical Society
Elec. Telegr. Rev.	The Electric Telegraph Review
Elec. World	Electrical World
Electrician	The Electrician
Electricite	l'Electricite
Electrochem. Met. Ind.	Electrochemical and Metallurgical Industry

Elektrochem. Zts.	Elektrochemische Zeitschrift
Elektrotech. Zts.	Electrotechnische Zeitschrift
Elliott Soc. J.	Journal of the Elliott Society of Natural History
Elliott Soc. Proc.	Proceedings of the Elliott Society of Natural History
Elsner, Mitth.	See Chem. Tech. Mitth.
Emden Naturf. Ges. Jahr.	...Jahresbericht der Natürforschenden Gesellschaft in Emden
Emden Naturf. Ges. Schr.	Kleine Schriften der Naturforschenden Gesellschaft in Emden
Eng.	Engineering
Eng. Contr.	Engineering and Contracting
Eng. Digest	Engineering Digest
Eng. Mag.	Engineering Magazine, The
Eng. Mining J. (Eng. Min. J.)	Engineering and Mining Journal, The
Eng. News	Engineering News
Eng. Record	Enginering Record, Building Record and Sanitary Engineer
Engineer	Engineer, The
Engineers' J.	The Engineers' Journal and Railway Gazette of India and the Colonies
Engineers Soc. Trans.	Society of Engineers. Transactions
Engl. Mech.	English Mechanic
Engler, Bot. Jahr.	Botanische Jahrbücher für Systematik, Pflanzengeschichte und Pflanzengeographie
Engrais, L'	Engrais, L'
Entom. Annual	The Entomologist's Annual
Entom. Mag.	The Entomological Magazine
Entom. Medd. (Kjobenh.)	Entomologiske Meddelelser udgivne af Entomologisk Forening
Entom. Month. Mag.	The Entomologist's Monthly Magazine
Entom. Nachr.	Entomologische Nachrichten
Entom. Record	The Entomologist's Record and Journal of Variation
Entom. Soc. Trans.	The Transactions of the Entomological Society of London
Entom. Tidskr.	Entomologisk Tidskrift pa Föranstaltande af Entomologiska Foreningen i Stockholm
Entomologica Amer.	Entomologica Americana
Entomologist	The Entomologist
E. P.	English (British) Patent
Epicure	Epicure, The
Epidem. Soc. Trans.	Transactions of the Epidemiological Society of London
Epinal (Vosges) Ann.	Annales de la Société d'Emulation du departement des Vosges
Erdel. Muz.-Egyl. Ertek.	Az Erdelyi Muzeum-Egylet Kiadvanyai Ertekezesek. (Publications of the Transylvanian Museum Association. Memoirs)
Erdmann, Sveriges Geol. Undersök.	Sveriges geologiska Undersökning, pa offentlig bekostnad, utförd under Ledning af A. Erdmann
Erfurt, Abh. Akad. Wiss.	Abhandlungen der Kurfürstlich Mainzer Akademie nützlicher Wissenschaften zu Erfurt
Erfurt, Akad. Jahr.	Jahrbücher der königlichen Akademie gemeinnütziger Wissenschaften zu Erfurt
Erfurt, Denkschr.	Denkschrift der Akademie gemeinnütziger Wissenschaften in Erfurt
Erfurt, Nova Acta	Nova Acta Academiae Electoralis Moguntinae Scientiarum utilium quae Erfurti est.

Ergeb. Physiol.	Ergebnisse der Physiologie, Wiesbaden
Erlangen, Abh.	Abhandlungen der Physikalisch-medicinischen Societät in Erlangen
Erlangen Anat. Inst.	See Bietr. Morphol.
Erlangen, Mitth. Phys. Med. Soc.	Wissenschaftliche Mittheilungen der Physikalisch-medicinischen Societät zu Erlangen
Erlangen Phys. Med. Soc. Sitzber.	Sitzungsberichte der Physikalisch-Medizinischen Societät zu (in) Erlangen
Erythea	Erythea. A Journal of Botany, West American and General
Essex Field Club Proc.	Journal of Proceedings of the Essex Field Club
Essex Field Club Spec. Mem.	Essex Field Club Special Memoirs
Essex Field Club Trans.	Transactions of the Essex Field Club
Essex Inst. Bull.	Bulletin of the Essex Institute
Essex Inst. Commun.	Communications read before the Essex Institute
Essex Inst. Proc.	Proceedings of the Essex Institute
Essex Natur. Hist. Soc. J.	Journal of the Essex County Natural History Society
Essex Natlist.	The Essex Naturalist
Essig. Ind.	Deutsche Essigindustrie
Etudes Gites Mineraux	See France Gites Min. Etudes
Eure, Bull. Acad. Ebroic.	Bulletin de l'Academie Ebroicienne
Eure, J. Agric.	Journal d'Agriculture, de Medicine et des Sciences accessoires
Eure, Recueil Trav.	Recueil des Travaux de la Société Libre d'Agriculture, des Sciences, des Arts et des Belles-Lettres du departmente de l'Eure
Eure, Soc. Agric. Bull.	Bulletin de la Société d'Agriculture, des Sciences, et des Arts du departement de l'Eure
Eure, Soc. Agric. Recueil	Recueil de la Société d'Agriculture, Sciences, Arts, et Belles-Lettres du departement de l'Eurs
Evkönyv	A' Magyar Tudos Tarsasag' Evkönyvei
Exner. Rep.	Repertorium der Physik.
Exper. Sta. Rec.	Experiment Station Record
Eyr	Eyr, et Medicinisk Tidsskrift
Fachgenosse	Fachgenosse, Der
Falaise, Mem. Soc. Acad.	Memoires de la Société Academique des Sciences, &c., de Falaise
Farben Ztg.	Farben Zeitung
Färb. Ztg.	Färber Zeitung (Lehne's)
Fechner Centr.	Centralblatt für Naturwissenschaften und Anthropologie
Fechner, Rep.	Repertorium der Experimental-Physik.
Fed. Inst. Min. Engin. Trans.	Transactions of the Federated Institution of Mining Engineers
Fer.	Ferrum, Halle
Ferussac, Bull. Sci. Math.	Bulletin des Sciences Mathematiques, Astronomiques, Physiques, et Chimiques par le Baron de Ferussac
Ferussac, Bull. Sci. Natur.	Bulletin des Sciences Naturelles et de Geologie
Feuille Jeunes Natur.	Feuille des Jeunes Naturalistes
Field Mus. Natur. Hist.	Field Museum of Natural History, Chicago, Publication
Fij. P.	Fiji Islands Patent
Fin. P.	Finland Patent
Finistere Soc. Sci. Bull.	Bulletin de la Société d'Etudes Scientifiques du Finistere
Finlande Soc. Geogr.	See Fennia
Finska Läk. Sällsk. Handl.	Finska Läkare Sällskapets Handlingar
Finska Vet.-Soc.	See Helsingfors, Bidrag. Helsingfors, Öfvers

Firenze Accad. Georgofili Atti	Atti della Reale Accademia Economico-Agraria dei Georgofili di Firenze
Firenze, Ann. Mus. Fis.	Annali del R. Museo di Fisica e Storia Naturale
Firenze, Ann. Mus. Imp.	Annali del Museo Imperiale di Fisica e Storia Naturale di Firenze
Firenze Congr. Bot. Atti	Atti del Congresso Internazionale Botanico tenuto in Firenze nel mese di Maggio 1874
Firenze, Mem. Soc. Ital.	See Modena
Firenze, Opusc. Sci.	Collezione d'Opuscoli scientifici.
Firenze R. Inst. Pubbl.	Pubblicazioni del R. Istituto di Studi Superiori Pratici e di Perfezionamento in Firenze
Firenze Soc. Georgofili Atti	Atti della (Real) Societa Economica di Firenze ossia de' Georgofili
Firenze Soc. Studi Geogr. Boll.	See Riv. Geogr. Ital.
Flora	Flora oder Allgemeine Botanische Zeitung
Flore Jardins	Annales d'Horticulture et de Botanique, ou Flore des Jardins du Royaume des Pays-Bas
Flore Serres	Flore des Serres et des Jardins de l'Europe
Florence	See Firenze
Flörke, Repert.	Repertorium des neuesten und wissenwürdigsten aus der gesammten Naturkunde
Földt. Közlön	Földtani Közlöny, Havi folyoirat kiadja a Magyarhoni Földtani Tarsulat
Folia Clin.	Folia clinica chimico et miscroscopica
Folia haematol.	Folia haematologica
Folia Therap. Lond.	Folia Therapeutica, London
Forbes, Med. Rev.	The British and Foreign Medical Review, or Quarterly Journal of Practical Medicine and Surgery
Forsch. Agr.-Phys.	Forschungen auf dem Gebiete der Agrikultur-Physik.
Förster, Allg. Bauztg.	Allgemeine Bauzeitung
Fortschr. Chem.	Fortschritte der Chemie, Physik und Physikalischen chemie
Fortschr. Med.	Fortschritte der Medicin.
Fortschr. Phys.	Die Fortschritte der Physik.
Fortschr. Röntgenstr.	Fortschritte auf dem Gebiete der Röntgenstrahlen
Fortschr. Theerfarben-Fabrikation	Fortschritte der Theerfarbenfabrikation und verwendter Industriezweige
Foundry	Foundry, The
F. P.	French Patent
France, Congr. Med. Chir.	Congres Medico-Chirurgicale de France
France, Congr. Sci.	Sessions des Congres Scientifiques de France
France Gites Miner. Etudes	Etudes des Gites Mineraux de la France
France, Inst. Provinces Annuaire	Annuaire de l'Institut des Provinces et des Congres Scientifiques de France
France, Inst. Provinces Mem.	Memoires de l'Institut des Provinces de France: Sciences physiques et naturelles
France Soc. Agric. Bull.	Bulletin des Seances de la Société Nationale d'Agriculture de France
France Soc. Agric. Mem.	Memoires publies par la Société Nationale d'Agriculture de France
France Soc. Bot. Bull.	Bulletin de la Société Botanique de France
France Soc. Entom.	See Abeille., Paris, Soc. Ent. Ann., Paris, Soc. Ent. Bull., Rev. Ent.
Franc Soc. Miner. Bull.	Bulletin de la Société Mineralogique de France. Bulletin de la Société Francaise de Mineralogie. (Ancienne Société Mineralogique de France)
France Soc. Zool.	See Paris, Caus. Sci.
France Soc. Zool. Bull.	Bulletin de la Société Zoologique de France

France Soc. Zool. Mem.	Memoires de la Société Zoologique de France
Frankfurt	See Senckenberg
Frankfurt, Jahr. Phys. Ver.	Jahrbuch zur Verbreitung naturwissenschaftlicher Kenntnisse, veranstaltet vom Physikalischen Verein zu Frankfurt a/Main
Frankf. Ver. Pflege Phot.	See Wien, Photogr. Correspond.
Frankfurt, Zool. Garten	Der Zoologische Garten Frankfurt a/M.
Frankfurter Zts. Pathol.	Frankfurter Zeitschrift für Pathologie
Französ. Ann.	Französische Annalen für die allgemeine Naturgeschichte, Physik, &c.
Freiberg, Jahr. Berg. Hütt.	Jahrbuch für den Berg- und Hüttenmann. Herausg. von der Königl. Berg-Akademie zu Freiberg
Freiburg, Beitr.	Beiträge zur Rheinischen Naturgeschichte
Freiburg, Ber.	Berichte über die Verhandlungen der Naturforschenden Gesellschaft zu Freiburg i. B.
Freie K.	Freie Künste
Frelon	Le Frelon. Journal d'Entomologie descriptive
Fries, Bot. Notiser	Botaniska Notiser
Froriep, Notizen	Notizen aus dem Gebiete der Natur- und Heilkunde
Fühling's Ztg.	Fühlings landwirtschaftliche Zeitung
Gac. ind.	La Gaceta industrial
Gand, Ann. Soc. Agric.	Annales de la Société Royale d'Agriculture et de Botanique
Gand, Ann. Soc. Med.	Annales de la Société de Medecine de Gand
Gand, Bull. Soc. Med.	Bulletin de la Société de Medecine de Gand
Gard, Apercu Trav.	Notice ou Apercu analytique des Travaux de l'Academie Royale du Gard
Gard, Mem. Acad.	Memoires de l'Academie du Gard
Gard, Notice Trav. Acad.	Notice des Travaus del'Academie du Gard
Garden & Forest	Garden and Forest. A Journal of Horticulture, Landscape Art and Forestry
Gardeners Chron.	The Gardeners Chronicle
Garnett, Ann. Phil.	Annals of Philosophy, Natural History, Chemistry &c.
Garten-Flora	Garten-Flora
Garten-Ztg.	Neue allgemeine Deutsche Garten- und Blumenzeitung
Gartenwelt	Gartenwelt, The
Gas World	Gas World, The
Gaz	Le Gaz
Gazz. del. Clin.	Gazzetta della Cliniche
Gazz. med. ital lomb.	Gazzetta medica italiana lombardia, Milano
Gazz. Chim. Ital.	Gazzetta Chimica Italiana
Geelong Field Natur. Club	See Wombat
Gehlen J.	Journal für dei Chemie und Physik
Gendrin, Trans. Med.	Transactions Medicales
Geneeskundig Mag.	Geneeskundig Magazijn
Geneve, Archiv.	See Archives Sci. Phys. Nat.
Geneve, Bull. Soc. Ornith Suisse.	Bulletin de la Societe Ornithologique Suisse
Geneve Conserv. Bot. Annuaire	Annuaire du Conservatoire du Jardin Botanique de Geneve
Geneve, Inst. Natl. Bull.	Bulletin de l'Institut National Genevois
Geneve, Inst. Natl. Mem.	Memoires de l'Institut National Genevois
Geneve, Mus. Hist. Natur. Ann.	See Rev. Suisse Zool.
Geneve, Recueil Trav. Soc. Med.	Recueil des Travaux de la Société Medicale de Geneve
Geneve, Soc. Geogr. Mem.	Memoires de la Société de Geographie de Geneve

Geneve, Soc. Phys. Mem.	Memoires de la Société de Physique et d'Histoire Naturelle de Geneve
Genie civ.	Genie Civil
Genova	See Congr. Bot. Int. Atti. 1892
Genova, Ann. Mus. Phys.	Annali del Museo Civico di Storia Naturale
Genova, Giorn.	Giornale degli Studiosi di Lettere, Science, arti e Mestieri
Genova, Mem. Accad.	Memoire dell'Accademia Imperiale delle Scienze di Genova
Genova, Mem. Ist. Ligure.	Memorie dell' Istituto Ligure
Genova, Mem. Soc. Med. Emul.	Memorie della Societa Medica di Emulazione di Genova
Genova Mus. Civ. Ann.	Annali del Museo Civico di Storia Naturale di Genova
Genova Mus. Zool. Anat. Comp. Boll.	Bollettino dei Musei di Zoologia e Anatomia Comparata della R. Universita di Genova
Genova, Soc. Ligust. Atti	Atti della Societa Ligustica di Scienze Naturali e Geografiche
Genova Univ. Atti	Atti della R. Universita di Genova
Geogr. Soc. J.	Journal of the Royal Geographical Society of London
Geogr. Soc. Proc.	Proceedings of the Royal Geographical Society and Monthly Record of Geography
Geogr. Soc. Suppl. Pap.	Royal Geograhical Society. Supplementary Papers
Geol. Mag.	Geological Magazine
Geol. Survey, Can.	Geological Survey, Canada
Gera, Naturwiss. Jahr.	Jahresbericht der Gesellschaft von Freunden der Naturwissenschaften in Gera, nebst Nachrichten über den Naturwissenschaftlichen Verein in Schleiz
Gerber	Der Gerber
Germar, Mag. Entom.	Magazin der Entomologie
Germar, Zts. Entom.	Zeitschrift für die Entomologie
Gergonne, Ann. Math.	Annales de Mathematique
Gesundh. Ing.	Gesundheits-Ingenieur
Gew. Ztg.	Wieck's Gewerbezeitung
Gewerbebl. Schw.	Schweizerisches Gewerbeblatt
Gewerbebl. Würt	Gewerbeblatt aus Württemberg
Gewerbeh.	Gewerbehalle
Gewerks Ztg.	Oesterreichische Gewerkszeitung
Giessen, Oberhess. Ges. Ber.	Berichte der Oberhessischen Gesellchaft für Natur- und Heilkunde
Gievel, Zts.	See Zts. Gesammt. Naturwiss.
Gilbert, Ann. Phys.	See Ann. Phys.
Gill. Tech. Micro. Repos.	Technical and Microscopical Repository
Giorn. Arcad.	Giornale Arcadico di Scienze
Giorn. farm. chim.	Giornale de farmacia, di chimica
Giorn. Gen. civ.	Giornale del Genio civile
Giron. Ist. Lomb.	See Bibl. Ital.
Giorn. Mineral. Crist. Petr.	Giornale di Mineralogia, Cristallografia e Petrografia
Gironde Comm. Meteorol.	See Bordeaux Soc. Sci. Mem.
Gironde, J. Med.	Journal Medical de la Gironde
Gistl, Faunus	Faunus
Glasgow. Inst. Engin. Trans.	Transactions of the Institution of Engineers and Shipbuilders in Scotland
Glasgow Med. Chir. Soc. Trans.	Transactions of the Medico-Chirurgical Society of Glasgow
Glasgow Med. J.	Glasgow Medical Journal
Glasgow Natur. Hist. Soc. Proc. & Trans.	Proceedings and Transactions of the Natural History Society of Glasgow
Glasgow Path. Clin. Soc. Trans.	Transactions of the Glasgow Pathological and Clinical Society

Glasgow Phil. Soc. Proc.	Proceedings of the Philosophical Society of Glasgow
Glashütte	Glashütte, Die
Glas-Ind.	Glas-Industrie, Die
Gleanings Sci.	Gleanings in Science
Globe	See Geneve Soc. Geogr. Mem.
Glückauf	Glückauf; Berg- und Hüttenmannische-Zeitschrift
Good Roads	Good Roads
Goodsir, Ann. Anat. Physiol.	Annals of Anatomy and Physiology
Gordon Coll. Phot. Assoc.	See Wombat.
Görlitz, Abh.	Abhandlungen der Naturforschenden Gesellschaft zu Görlitz
Götheborg, Handl.	Götheborgs Kongl. Vetenskaps och Vitterhets Samhälles Handlingar
Götheborg, Nya Handl.	Nya Handlingar af Kongl. Vettenskaps och Vitterhets Samhallet i Götheborg
Göttingen, Abh.	Abhandlungen der Königlichen Gesellschaft der Wissenschaften zu Göttingen
Göttingen, Comment.	Commentationes recentiores Societatis, etc.
Göttingen, Nachr.	Nachrichten von der Georg-Augusts Universität und der Königl. Gesellschaft der Wissenchaften zu Göttingen
Göttinger Studien	Göttinger Studien
Göttingen, Studien Ver.	Studien des Göttingischen Vereins Bergmännischer Freunde
Gräfe, J. Chir. Augenheilk.	Journal der Chirurgie und Augen-Heilkunde
Graph. Mitth.	Schweizer graphische Mitteilungen
Graubünden Naturf. Ges. Jahr.	Jahresbericht der Naturforschenden Gesellschaft Graubündens
Gravenhage, Athenaeum	Athenaeum
Gravenhage, Inst. Ingen. Tijdschr.	Tijdschrift van het Koninklijk Instituut van Ingenieurs
Gravenhage, Inst. Ingen. Uittrek.	Uittreksels uit Vreemde Tijdschriften voor de Leden van het Koninklijk Instituut van Ingenieurs
Gravenhage, Inst. Ingen. Verh.	Verhandelingen van het Koninklijk Instituut van Ingenieurs
Gravenhage, Inst. Ingen. Verslag.	K. Instituut van Ingenieurs. Algemeen Verslag van de Werkzaamheden en Notulen der Vergaderingen
Gravenhage, Tijdschr.	Tijdschrift voor Entomologie, door de Nederlandsche Entomologische Vereeniging
Graves, Natur. J.	The Naturalists' Journal and Miscellany
Graz Bot. Inst. Mitth.	Mittheilungen aus dem Botanischen Institute zu Graz
Graz, Unters. Physiol. Histol.	Untersuchungen aus dem Institute für Physiologie und Histologie
Great. Brit. Phil. Soc.	See Victoria Inst. J.
Greifswald Naturwiss. Ver. Mitth.	See Neu-Vorpommern Mitth.
Grenoble, Acad. Delph. Bull.	Bulletin de l'Academie Delphinale, ou Société des Sciences et Arts de Grenoble
Grevillea	Grevillea, a Quarterly Record of Cryptogamic Botany and its Literature
Groningen, Ann. Acad.	Annales Academiae Groninganae
Gruithuisen, Neue Analekt.	Neue Analekten für Erd- und Himmels-kunde
Grunert Archiv.	Archiv für Mathematik und Physik
Grunert, Meteor. Optik	Beiträge zur meteorologischen Optik, etc.
Guat. P.	Guatemala Patent

Guia Minero	Guia del Minero: Periodico cientifico, industrial y mercantil
Guillemin, Archiv. Bot.	Archives de Botanique, ou Recueil Mensuel de Memoires originaux, etc.
Gummi-Ztg.	Gummi-Zeitung
Günsburg, Zts. Klin. Med.	Zeitschrift für klinische Medizin, mit dem Verein für physiologische Heilkunde in Breslau
Gurlt, Mag. Ges. Thierheilk.	Magazin für die gesammte Thier-Heilkunde
Guy's Hosp. Rep.	Guy's Hospital Reports
Haarlem Kolon. Mus. Bull.	Bulletin van het Koloniaal Museum te Haarlem
Haarlem, Mus. Teyler Archiv.	Archives du Musee Teyler
Haarlem, Natuurk. Verh. Maatsch. Wet.	Natuurkundige Verhandelingen van de (Bataafsch) Hollandsche Maatschappij der Wetenschappente Haarlem
Haaxman, Tijdschr.	Tijdschrift voor Wettenschappelijke Pharmacie, etc.
Habana Acad. Anales.	Anales de la (Real) Academie de Ciencias Medicaes Fisicas y Naturales de la Habana
Haeser, Archiv. Med.	Archiv für die gesammte Médicin
Hage	See Gravenhage
Hahnemann. Month.	Hahnemannian Monthly, Philadelphia
Haidinger, Abh.	Naturwissenschaftliche Abhandlungen
Haidinger, Ber.	Berichte über die Mittheilungen von Freunden der Naturwissenschaften in Wien
Hainaut Soc. Mem.	Memoires et Publications de la Société des Sciences, des Arts et des Lettres du Hainaut
Hall, Bijdragen	Bijdragen tot de Natuurkundige Wetenschappen
Halle, Abr. Naturwiss. Ver.	Abhandlungen des Naturwissenschaftlichen Vereins für Sachsen und Thüringen in Halle
Halle aux cuirs, La	Halle aux cuirs, La
Halle, Jahr. Naturwiss. Ver.	Jahresbericht des Naturwissenshaftlichen Vereins in Halle
Halle Kryptog. Lab.	See Beitr. Physiol. Morphol.
Halle, Naturf. Ges. Abh.	Abhandlungen der Naturforschenden Gesellschaft zu Halle
Halle, Naturf. Ges. Ber.	Bericht der Naturforschenden Gesellschaft zu Halle
Halle, Naturf. Ges. Neu. Schr.	Neue Schriften der Naturforschenden Gesellschaft zu Halle
Halle, Zts. Ges. Naturwiss.	Zeitschrift für die gesammten Naturwissenschaften
Hamburg, Abh. Geb. Naturwiss.	Abhandlungen aus dem Gebiete der Naturwissenschaften
Hamburg Bot. Ges.	See Bot. Centrbl.
Hamburg, Mitth.	Mittheilungen aus den Verhandlungen der Naturwissenschaftlichen Gesellschaft in Hamburg
Hamb. Mus. Ber.	Naturhistorisches Museum zu Hamburg. Berichte
Hamb. Mus. Jahr.	Jahresbericht über das Naturhistorische Museum zu Hamburg
Hamb. Mus. Mitth.	Mittheilung aus dem Naturhistorischen Museum in Hamburg
Hamb. Naturwiss. Ver. Abh.	Abhandlungen aus dem Gebiete der Naturwissenschaften herausgegeben vom Naturwissenschaftlichen Verein in Hamburg
Hamb. Ver. Naturwiss. Unterh. Verh.	Verhandlungen des Vereins für Naturwissenschaftliche Unterhaltung zu Hamburg
Hamb. Wiss. Anst. Jahr.	Jahrbuch der Hamburgischen Wissenschaftlichen Anstalten

Hampshire Field Club Pap. & Proc.	Papers and Proceedings of the Hampshire Field Club
Hannover Architekt.-Ver. Zts.	Zeitschrift des Architekten- und Ingenieur-Vereins zu Hannover. Zeitschrift für Architektur und Ingenieurwesen
Hannover Jahr.	...Jahresbericht der Naturhistorischen Gesellschaft zu Hannover
Hannöverische Ann.	Hannöverische Annalen für die gesammte Heilkunde
Harlem Soc. Holland. Sci.	See Arch. Neerland
Hartford, Trans.	Transactions of the Natural History Society of Hartford
Harvard Mus. Zool. Mem.	Memoirs of the Museum of Comparative Zoology at Harvard College
Harvard Mus. Zool. Bull.	Bulletin of the Museum of Comparative Zoology at Harvard College, in Cambridge
Harz, Naturwiss. Ver. Ber.	Berichte des Naturwissenschaftlichen Vereins des Harzes zu Blankenburg
Havre, Cercle Bot.	Cercle pratique d'Horticulture et de Botanique de l'arrondissement du Havre: Bulletins
Haw. P.	Hawaiian Patent
Haye	See Congr. Int. Hyg. C. R., 1884
Heart	Heart
Hedwigia	Hedwigia. Ein Notizblatt für Kryptogamische Studien nebst Repertorium für Kryptogamische Literatur. Hedwigia. Organ für (specielle) Kryptogamenkunde (und Phytopathologie) nebst Repertorium für (Kryptogamische) Literatur.
Heidelb. Jahr. Lit.	Jahrbücher der Literatur. Verhandlungen des Naturhistorisch-Medicinischen Vereins zu Heidelberg
Heidelb. Naturhist. Med. Festschr.	Festchrift zur Feier des fünfhundertjährigen Bestehens der Ruperto-Carola dargebracht von dem Naturhistorisch-Medicinischen Verein zu Heidelberg
Heidelb. Naturhist. Med. Verh.	Verhandlungen des Naturhistorisch-Medicinischen Vereins au Heidelberg
Heidelb., Verh.	Verhandlungen der in Heidelberg versammelten Augenärzte
Heis, Wochenschr.	Wochenschrift für Astronomie, Meteorologie, und Geographie
Heller, Archiv.	Archiv für physiologische und pathologische Chemie und Mikroskopie
Helsingfors, Acta Soc. Sci. Fenn.	Acta Societatis Scientiarum Fennicae
Helsingfors, Bidrag Finlands Natur o. Folk.	Bidrag till kannedom om Finlands Natur och Folk, utgifna af Finska Vetenskaps-Societeten
Helsingfors, Bidrag Finlands Naturkänn.	Bidrag till Finlands Naturkännedom, Etnografi och Statistik, utgifna af Finska Vetenskaps-Societeten
Helsingfors, Faun. Flor. Fenn. Acta.	Acta Societatis pro Fauna et Flora Fennica
Helsingfors, Fauna Flora Fenn. Medd.	Meddelanden af Societas pro Fauna et Flora Fennica
Helsingfors, Faun. Flor. Fenn. Notiser	Notiser ur Sällskapets pro Fauna et Flora Feennica Förhandlingar
Helsingfors, Öfvers, Finaka Vet. Soc.	Öfversigt af Finska Vetenskaps-Societatens Förhandlingar
Helv. Chim. Acta	Helvetica Chimica Acta
Henle und Pfeufer, Zts.	See Zeitschrift für rationelle Medicin
Hermannstader Verh.	Verhandlungen und Mittheilungen des Siebenbürgischen Vereins für Naturwissenschaften in Hermannstadt

Hermbstätt, Archiv.	Archiv der Agriculturchemie für denkende Landwirthe
Hermstädt, Bull.	Bulletin des Neuesten und Wissenwürdigsten aus der Naturwissenschaft, etc.
Hermbstädt, Museum	Museum des Neuesten und Wissenwürdigsten aus dem Gebiete der Naturwissenschaft, der Künste, der Fabriken, der Manufakturen, der technischen Gewerbe, der Landwirthschaft, der Produktenwaaren und Handelskunde, und der bürgerlichen Haushaltung, &c.
Hertha	Hertha
Herts. Natur. Hist. Soc. Trans.	Transactions of the Hertfordshire Natural History Society and Field Club
Hessen, Naturhist. Verg.	Verhandlungen des Naturhistorischen Vereins für das Gross herzogthum Hessen und Umgebung
Heusinger, Zts.	Zeitschrift für die organische Physik
Hide and Leather	Hide and Leather
High Wycombe Natur. Hist. Mag.	The Quarterly Magazine of the High Wycombe Natural History Society
Highland Soc. Trans.	Transactions of the Highland and Agricultural Society of Scotland with an abstract of the Proceedings
Hildesheim Roemer-Mus. Mitth.	Mittheilungen aus dem Roemer-Museum Hildesheim
Himly, Bibl. Ophthalm.	Bibliothek für Ophthalmologie
Hippone	See Bone
Hisinger, Afh.	Afhandlingar i Fysik, Kemi, och Mineralogie
Hobart Town	See Tasmania
Hoeven en Vriese, Tijdschr.	Tijdschrift voor Natuurlijke Geschiedenis en Physiologie
Hoff, Mag.	Magazin für die gesammte Mineralogie, Geognosie, etc.
Hoffman, Phytogr. Blätt.	Phytographische Blätter
Holl. P.	Holland Patent
Holländ, Beitr.	Holländsiche Beiträge zu den anatomischen und physiologischen Wissenscaften
Holländ, Mag.	Holländisches Magazin der Naturkunde
Holmesdale Natur. Hist. Club Proc.	Proceedings and Annual Reports of the Holmesdale Natural History Club, Reigate, for the years 1865–67
Homme	L'Homme: Journal illustre des Sciences Anthropologiques
Hooker, Bot. Miscell.	The Botanical Miscellany
Hooker, Comp. Bot. Mag.	Companion to the Botanical Magazine
Hooker, Lond. J. Bot.	London Journal of Botany
Hoppe, Bot. Taschenb.	Neues Botanisches Taschenbuch für die Anfänger dieser Wissenschaft und der Apothekerkunst
Horae Soc. Entom. Rossicae	Horae Societatis Entomologicae Rossicae variis sermonibus Rossicae usitatis
Horkel, Archiv.	Archiv. für die thierische Chemie
Horn, Archiv. Med.	Archiv. für praktische Medizin und Klinik
Horn's Phot. J.	Horn's photographisches Journal
Hornschuch, Archiv.	Archiv Skandinavischer Beiträge zur Naturgeschichte
Horolog. J.	The Horological Journal
Hortic. Soc. J.	Journal of the Royal Horticultural Society of London
Hortic. Soc. Trans.	Transactions of the Horticultural Society of London
Hufeland, J. Arzn.	Journal der practischen Arzneikunde
Humboldt.	Humboldt. Monatsschrift für die Gesamten Naturwissenschaften
Humming Bird	The Humming Bird. .... scientific, artistic and industrial Review

Hongkong P.	Hongkong Patent
Hung. P.	Hungarian Patent
Hutm. Ztg.	Deutsche Hutmacher-Zeitung
Hyg. Congr.	See Congr. Int. Hig. Act.; Congr. Int. Hyg. C. R.; Int. Congr. Hyg. Arb.; Int. Congr. Hyg. Trans.
Hyg. Rundschau.	Hygienische Rundschau. Berlin
Hyg. viande	Hygiene de la viande et du lait, L'
Iekaterinenb., Soc. Oural. Bull.	Bulletin de la Société Ouralienne d'Amateurs des Sciences Naturelles
Il Berico	Il Berico
Il Cimento	Il Cimento
Il. Giamb-Vico	Il Giambattista-Vico
Il Progresso	Il Progresso delle Scienze, Lettere, ed Arti.
Il Subalpino	Il Subalpino, Giornale di Scienze
Il Tempo	Il Tempo, Giornale Italiano di Medicina
Ill. Insects Rep.	...Report of the State Entomologist...on the Noxious and Beneficial Insects of the State of Illinois
Ill. Lab. Natur. Hist. Bull.	Bulletin of the Illinois State Laboratory of Natural History
Ill. Mus. Natur. Hist. Bull.	Bulletin...of the Illinois State Museum of Natural History
Illiger, Magazin	Magazin für Insektenkunde
Illumin. Engin. (London)	Illuminating Engineer (London), The
Illust. Hortic.	Illustration horticole; journal special des Serres et des Jardins
Illust. landw. Ztg.	Illustrierte landwirtschaftliche Zeitung
Illust. Off. J.	Illustrated Official Journal, The (Patents)
Illust. Wochenschr. Entom.	Illustrierte Wochenschrift für Entomologie. Internationales Organ für alle Interessen der Insektenkunde. Offizielles Organ der Berliner Entomologischen Gesellschaft
Impr.	L'imprimerie
Ind. Chim.	Industria chimica
Ind. lait.	L'Industrie laitiere
Ind. Text.	L'industrie textile
Ind. Ztg.	Deutsche Industrie Zeitung
Index Med.	Index Medicus, Washington
India Agric. Soc. J.	Journal of the Agricultural and Horticultural Society of India
India, Agric. Soc. Proc.	Proceedings of the Agricultural and Horticultural Society of India
India Agric. Soc. Trans.	Transactions of the Agricultural and Horticultural Society of India
India Bot. Surv. Records	Records of the Botanical Survey of India
India Dept. Agric.	India Department of Agriculture, Publications
India, Govt. Records (For. Dept.)	Selections from the Records of the Government of India. (Foreign Department)
India, Govt. Records (Home Dept.)	Selections from the Records of the Government of India
India P.	Indian Patent
India Rev.	India Review and Journal of Foreign Science and the Arts
India Rub. J.	India Rubber Journal
India Rub. World	India Rubber World
Indian Ann.	Indian Annals of Medical Science
Indian J. Med. Phys. Sci.	Indian Journal of Medical Science
Indian Med. Gaz.	The Indian Medical Gazette, a monthly record of Medicine, &c.

Indian Meteorol. Mem.	Indian Meteorological Memoirs: being occasional Discussions and Compilations of meteorological data relating to India and the neighboring countries
Indian Mus. Notes	Indian Museum Notes
Industrieztg. Ungarn	Industriezeitung für Ungarn
Ingenieur	Der Ingenieur
Inghirami, Opuscoli	Nuova Collezione di Opuscoli e Notizie di Scienze
Innsbruck, Jahr.	Jahresbericht der k. k. Ober-Realschule zu Innsbruck
Innsbruck Naturwiss. Med. Ber.	Berichte des Naturwissenschaftlich-medizinischen Vereines in Innsbruck
Innsbruck, Neue Zts.	Neue Zeitschrift des Ferdinandeums für Tirol
Innsbruck, Zts. Ferdinandeums	Zeitschrift des Ferdinandeums für Tirol und Voralberg
Inst.	L'Institut
Inst. Act. J.	Journal of the Institute of Actuaries (and Assurance Magazine)
Inst. Brewing Trans.	Transactions of the Institute of Brewing
Inst. Civ. Eng. Proc.	Minutes of the Proceedings of the Institution of Civil Engineers
Inst. Egypt. Bull.	Bulletin de l'Institut Egyptien
Inst. Egypt. Mem.	Memoires (ou Travaux originaux) presentes (et lus) a l'Institut Egyptien
Inst. Elect. Engin. J.	Journal of the Institution of Electrical Engineers
Inst. Mechan. Engin. Proc.	Institution of Mechanical Engineers. Proceedings
Inst. Min. Eng. Trans.	Transactions of the Institution of Mining Engineers
Inst. Min. Met. Trans.	Transactions of the Institution of Mining and Metallurgy
Inst. Solvay Trav.	Institut Solvay. Travaux de Laboratoire
Intell. Observer	The Intellectual Observer
Intl. Beitr. Path. Therap.	Internationale Beiträge zur Pathologie und Therapie, die Ernährungsstörungen, Stoffwechsel und Verdauungkrankheiten
Intl. Congr. Appl. Chem.	International Congress of Applied Chemistry
Intl. Congr. Hyg. Trans.	Transactions of the International Congress of Hygiene and Demography
Intl. Congr. Zool. Proc.	Proceedings International Congress of Zoology
Intl. Entom.-Ver.	See Zürich, Soc. Ent.
Intl. Med. Congr. Trans.	Transactions of the International Medical Congress
Intl. Med. Congr. Verh.	Verhandlungen des Internationalen Medicinischen Congresses
Intl. J. Anat.	Monthly International Journal of Anatomy and Histology (Physiology)
Intl. Mschr. Anat.	See Intl. J. Anat.
Intl. Sugar J.	International Sugar Journal, The
Intl. Zentr. Baukeram. Glasind.	Internationales Zentralblatt für Baukeramik und Glasindustrie
Intl. Zts. Metallog.	Internationale Zeitschrift für Metallographie
Invent. Rec.	Inventor's Record, The
Iowa Acad. Sci. Proc.	Proceedings of the Iowa Academy of Sciences
Iowa Univ. Lab. Natur. Hist. Bull.	Bulletin from the Laboratories of Natural History of the State University of Iowa
Ireland, Coll. Physicians Trans.	Transactions of the Association of Fellows and Licentiates of the King's and Queen's College of Physicians in Ireland
Ireland, Inst. Civ. Eng. Trans.	The Transactions of the Institute of Civil Engineers of Ireland

Ireland Roy. Soc. Ant. Proc. & Pap.	See Dublin, Roy. Soc. Ant. Ir. Jl.
Ireland Zool. Soc.	See Irish Natlist
Iris	Correspondenz-Blatt des Entomologischen Vereins Iris zu Dresden. Iris, Dresden. Deutsche Entomologische Zeitschrift herausgegeben von der Gesellschaft Iris zu Dresden in Verbindung mit der Deutschen Entomologischen Gesellschaft zu Berlin.. Fortsetzung des "Correspondenz-Blattes des Entomologischen Vereins Iris."
Irish Acad. Cunningham Mem.	Royal Irish Academy. Cunningham Memoirs
Irish Acad. Proc.	Proceedings of the Royal Irish Academy
Irish Acad. Trans.	The Transactions of the Royal Irish Academy
Irish Natur.	The Irish Naturalist: a monthly Journal of general Irish Natural History
Iron	Iron
Iron Age	Iron Age
Iron Coal Trades Rev.	Iron Coal Trades Review
Iron Steel Inst. J.	The Journal of the Iron & Steel Institute
Iron Steel Inst. Trans.	Transactions of the Iron and Steel Institute
Isenflamm, Beitr. Zerglied.	Beiträge für die Zergliederungskunst
Isere Soc. Bull.	Bulletin de la Société de Statistique, des Sciences naturelles et des Arts industriels du Departement de l'Isere
Isle of Man Natur. Hist. & Antiq. Soc.	See Yn Lioar Manninagh
Ital. P.	Italian Patent
Italia, Soc. Bot. Bull.	Bullettino della Societa Botanica Italiana
Italia Soc. Crittog. Atti	Atti della Societa Crittogamologica Italiana
Italia Soc. Crittog. Comment.	Commentario della Societa Crittogamologica Italiana
Italia Soc. Crittog. Mem.	Memorie della Societa Crittogamologica Italiana
Italia, Soc. Entom. Bull.	Bullettino della Societa Entomologica Italiana
Italia, Soc. Zool. Boll.	Bollettino della Societa Zoologica Italiana
Ithaca, Cornell Univ. Bull. Amer. Paleont.	Bulletins of American Paleontology
J.	Journal
J. A. C. S.	Journal of the American Chemical Society
J. Adv. Therap.	Journal of Advanced Therapeutics, New Yozk
J Agric.	The (Quarterly) Journal of Agriculture
J. agric. Hort.	Journal de l'Agriculture, le Horticulture, etc.
J. Agric. Prat.	Journal d'Agriculture pratique, etc.
J. Agric. Sci.	Journal of Agricultural Science
J. agric. Soc.	Journal of the Agricultural Society
J. Agric. Tropicale	Journal d'Agriculture tropicale
J. allied Soc.	Journal of the Allied Societies (Dental)
J. Amer. Lea. Chem. Assoc.	Journal of the American Leather Chemists' Association
J. Amer. Med. Assoc.	Journal of the American Medical Association
J. Amer. Pharm. Assoc.	Journal of the American Pharmaceutical Association
J. Amer. Soc. Mechan. Eng.	Journal of the American Society of Mechanical Engineers
J. Anal. Chem.	The Journal of Analytical (and Applied) Chemistry
J. Anat.	Journal de l'anatomie de la Physiologie normales et pathologiques de l'homme et des animaux
J. Anat. Physiol.	The Journal of Anatomy and Physiology
J. Appl. Chem.	Journal of Applied Chemistry

J. Appl. Micr.	Journal of Applied Microscopy
J. Assoc. Eng. Soc.	Journal of the Association of Engineering Societies
J. Biol. Chem.	Journal of Biological Chemistry
J. Bot.	Journal de Botanique
J. Buchdr.	Journal für Buchdruckerkunst
J. C. S.	Journal of the Chemical Society, London
J. Camera Club	Journal of the Camera Club
J. Can. Min. Inst.	Journal of the Canadian Mining Institutes
J. Chem. Met. Soc. South Af.	Journal of the Chemical, Metallurgical and Mining Society of South Africa
J. chim. med.	Journal de chimie medicale, de pharmacie et de toxicologie
J. chim. phys.	Journal de chimie, physique, electrochemie, thermochimie, radiochimie, mechanique, chimie, stoichiometrie
J. Chir.	Journal de Chirurgie
J. Chir. Augenheilk.	Journal der Chirurgie und Augenheilkunde
J. Coll. Agric. Imp. Univ. Tokyo	Journal of the College of Agriculture, Imperial University of Tokyo
J. Comp. Path. Therap.	The Journal of Comparative Pathology and Therapeutics
J. Conch.	The Journal of Conchology
J. ecole poly.	Journal de l'Ecole polytechnique
J. Entom.	Journal of Entomology, descriptive and geographical
J. Exp. Med.	Journal of Experimental Medicine
J. Exp. Zool.	Journal of Experimental Zoology, The
J. fabr. sucre	Journal des fabricants de sucre
J. Frank. Inst.	Journal of the Franklin Institute
J. Gasbeleucht	Journal für Gasbeleuchtung
J. Gaslighting	Journal of Gas Lighting
J. Gen. Physiol.	Journal of General Physiology
J. Genie Civ.	Journal du Genie Civil des Sciences et des Arts
J. Geol.	Journal of Geology
J. Goldschm.	Journal der Goldschmiedekunst und verwandter Gewerbe
J. Heb. Med.	Journal Hebdomadaire de Medecine
J. Heb. Sci. Med.	Journal Hebdomadaire des Progres des Sciences et Institutions Medicales
J. Home Econ.	Journal of Home Economics, The
J. Hygiene	Journal of Hygiene
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry
J. Indian Archipel.	Journal of the Indian Archipelago and Eastern Asia
J. Infect. Dis.	Journal of Infectious Diseases
J. Inst. Brewing	Journal of the Institute of Brewing
J. Inst. Metals	Journal of the Institute of Metals
J. Intl. Anat.	See Int. J. Anat.
J. Invent.	Journal des Inventeurs
J. Landw.	Journal für Landwirtschaft
J. Med. Chir. Pharm.	Journal de Medecine, Chirurgie, Pharmacie
J. Med. Paris	Journal de medicine de Paris
J. Med. Research	Journal of Medical Research
J. Microgr.	Journal de micrographie
J. Micro. Sci.	Quarterly Journal of Microscopical Science
J. Mines	Journal des Mines, ou Recueil de Memoires sur l'exploitation des Mines, et sur les Sciences et les Arts qui s'y rapportent
J. mines met.	Journal des mines et de metallurgie
J. Morphol.	Journal of Morphology

J. Mus. Godeffroy	Journal des Museum Godeffroy. Geographische, Ethnographische und Naturwissenschaftliche Mittheilungen
J. Mycol.	The Journal of Mycology
J. N. Engl. Water Works Assoc.	Journal New England Water Works Association
J. Opthalmol.	Journal d'Ophthalmologie
J. Ornith.	Journal für Ornithologie
J. Papier	Journal de Fabricants de Papier, fonde et publie par L. Piette
J. Path. Bact.	The Journal of Pathology and Bacteriology
J. Petrole	Journal du petrole
J. Pharm.	Journal de Pharmacie
J. Pharm. Anvers	Journal de Pharmacie d'Anvers
J. Pharm. Chim.	Journal de Pharmacie et de Chimie
J. Pharm. Elsass-Lothringen	Journal de pharmacie von Elsass-Lothringen
J. Pharm. Soc. Japan	Yakagakuzasshi (Journal of the pharmaceutical society of Japan)
J. Pharmacol.	Journal of Pharmcology and Experimental Therapeutics
J. Phot. Suppl.	Journal of Photographic Supplies
J. Phot. Soc.	Journal of the Photographic Society
J. Phys.	Journal de Physique theorique et appliquee
J. Phys. Chem.	The Journal of Physical Chemistry
J. Phys. Chim.	Journal de Physique, de Chimie, et de l'Histoire Naturelle
J. Physiol.	The Journal of Physiology
J. physiol. path. gen.	Journal de physiologie et de pathologie general, Paris
J. prakt. Chem.	Erdmann's Journal für praktische Chemie
J. Psychol. Med.	Journal of Psychological Medicine and Mental Pathology
J. Roy. Agric. Soc.	Journal of the Royal Agricultural Society
J. Roy. Astron. Soc. Canada	Journal of the Royal Astronomical Society of Canada
J. Roy. Inst. Pub. Health	Journal of the Royal Institute of Public Health
J. Roy. San. Inst.	Journal of the Royal Sanitary Institute
J. Roy. Soc. N. S. Wales	Journal of the Royal Society of New South Whales
J. Roy. U. S. Inst.	Journal Royal United Service Institution
J. Russ. Phys. Chem. Soc.	Journal of the Russian Physical Chemical Society
J. S. C. I.	Journal of the Society of Chemical Industry
J. Savants	Journal des Savants
J. Sci.	The Journal of Science
J. sci. math. physi. nat.	Journal de sciencias mathematicas, physicas naturaes
J. Soc. Arts	Journal of the Royal Society of Arts
J. Soc. Dyers Col.	Journal of the Society of Dyers and Colorists
J. soc. pharm. Anvers	Journal de pharmacie, organe de la société de pharmacie d'Anvers
J. Soc. Telegr. Eng.	Journal of the Society of Telegraphic Engineers
J. State Med.	The Journal of State Medicine
J. suisse chim. pharm.	Journal suisse de chimie et pharmacie
J. Travel	The Journal of Travel and Natural History
J. Trop. Med.	The Journal of Tropical Medicine
J. U. S. Artill.	Journal of the United States Artillery
J. Univ. Med.	Journal universel et hebdomadaire de Medecine et de Chirurgie pratiques et des Institutions medicales
J. Univ. Sci. Med.	Journal Universel des Sciences Medicales
J. Wash. Acad. Sci.	Journal of the Washington Academy of Sciences
J. Western Soc. Eng.	Journal of the Western Society of Engineers

Jaarb. Mijnw. Nederl. Ind.	Jaarboek van het Mijnwezen in Nerderlandsch Oost-Indie
Jahr. = Jahresbericht	Jahrbuch
Jahr. Agrik.-Chem.	Jahresbericht über die Fortschritte der Agrikulturchemie mit besonderer Berücksichtigung der Pflanzenchemie und Pflanzenphysiologie
Jahr. Berg- u. Hüttenw.	Jahrbuch für das Berg- und Hüttenwesen im Königreiche Sachsen
Jahr. Kinderheilk.	Jahrbuch für Kinderheilkunde und physische Erziehung
Jahr. Chem.	Jahresbericht der Chemie (Liebig-Kopp)
Jahr. Gähr. Organ.	Jahresbericht über die Fortschritte in der Lehre von den Gährungs-Organismen (Koch)
Jahr. Mineral.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie
Jahr. Mineral Beil.-Bd.	Neues Jahrbuch für Mineralogie, Geologie, und Palaeontologie, Beilage-Band
Jahr. Pharm.	Jahresbericht der Pharmacie
Jahr. Phot.	Jahrbuch der Photographie (Eder)
Jahr. Phot. Reprod.	Jahrbuch für Photographie und Reproduktiontechnik
Jahr. Phy. Ver. Frankfurt	See Frankfurt, Jahr. Phys. Ver.
Jahr. Physiol.	Jahresbericht über die Fortschritte der Physiologie
Jahr. Radioactiv. Electronik.	Jahrbuch der Radioaktivität und Electronik
Jahr. rein. Chem.	Jahresbericht der reinen Chemie
Jahr. Tier-Chem.	Jahresbericht über der Fortschritte der Tier-Chemie
Jahr. wiss. Bot.	Jahrbücher für wissenschaftliche Botanik
Jamaica Inst. J.	Journal of the Institute of Jamaica
Jamaica P.	Jamaica Patent
Jamaica Soc. Arts. Trans.	Transactions of the Jamaica Society of Arts
Jamain, Archives Ophthalm.	Archives d'Ophthalmolgie
Jap. P.	Japanese Patent
Jardine, Mag. Zool. Bot.	The Magazine of Zoology and Botany
Jena Ann. Acad.	Annales Academiae Jenensis
Jena Ann. Phys. Med.	Die Jenaischen Annalen für Physiologie und Medicin
Jena Ann. Soc. Mineral	Annalen der Societät für die gesammte Mineralogie zu Jena
Jena Denkschr.	Denkschriften der Medicinisch-Naturwissenschaftlichen Gesellschaft zu Jena
Jena Geogr. Ges. Mitth.	Mittheilungen der geographischen Gesellschaft (für Thüringen) zu Jena
Jena Sitzber.	Sitzungsberichte der Jenaischen. Gesellschaft für Medicin und Naturwissenschaft
Jena Zts.	Jenaische Zeitschrift für Naturwissenschaft herausgegeben von der Medicinisch-naturwissenschaftlichen Gesellschaft zu Jena
Jern-Kontoret's Ann.	Jern-Kontoret's Annaler
Johns Hopkins Biol. Lab. Mem.	Memoirs from the biological laboratory of the Johns Hopkins University
Johns Hopkins Biol. Lab. Stud.	Johns Hopkins University. Studies from the Biological Laboratory
Johns Hopkins Univ. Circ.	The Johns Hopkins University Circulars
Jura, Trav. Soc. Emul.	Travaux de la Société d'Émulation du Department du Jura
Jurjew	See Dorpat
Just's bot. Jahr.	Just's botanischer Jahresbericht, Leipzig and Berlin
Kali	Kali

Kampen, Mag.	Magazin voor Wetenschappen, Kunsten, &c.
Kan. Acad. Sci. Trans.	Transactions of the....annual meeting of the Kansas Academy of Science
Kan. Univ. Quart.	The Kansas University Quarterly
Karlsruhe Bact. Inst. Arb.	Arbeiten aus dem bacteriologischen Institut der technischen Hochschule zu Karlsruhe
Karlsruhe Naturwiss. Ver. Verh.	Verhandlungen des Naturwissenschaftlischen Vereins in Karlsruhe
Kärnten, Berg-Verein, Zts.	Zeitschrift des Berg- u. Hüttenmännischen Vereins für Kärnten
Kärnten Landesmus. Jahr.	Jahrbuch des naturhistorischen Landes-Museums von Kärnten
Kärnten, Zts.	Zeitschrift des berg- und hüttenmännischen Vereines für Kärnten
Karsten	See Botan. Untersuch.
Karsten, Archiv.	Archiv für Mineralogie, Geognosie, Bergbau, und Hüttenkunde
Kassel Ver. Naturk. Ber.	Bericht des Vereins für Naturkunde zu Cassel
Kassel Ver. Naturk. Festschr.	Festschrift des Vereins für Naturkunde zu Cassel zur Feier seines Fünfzigjährigen Bestehens
Kastner, Archiv. Chem.	Archiv. für Chemie und Meteorologie
Kastner, Archiv. Naturlehre	Archiv. für die gesammte Naturlehre
Kazan Soc. Phys.-Math. Bull.	Bulletin de la Société Physico-Mathematique de Kazan
Kazan Soc. Natur. Proc.	Proceedings of the Physico-Mathematical Section of the Society of Naturalists of the Imperial University of Kazan
Kazan Soc. Natur. Trans.	Transactions of the Society of Naturalists of the Imperial University of Kazan
Kazan Univ. Bull.	Bulletin of the Imperial University of Kazan
Kazan Univ. Mem.	Scientific Memoirs of the Imperial University of Kazan
Kekule, Krit. Zts. Chem.	Kritische Zeitschrift für Chemie, Physik, und Mathematik; see also Zts. Chem.
Keram. Rundschau	Keramische Rundschau
Kew Bull.	Royal (Botanic) Gardens, Kew. Bulletin of Miscellaneous Information
Kharkov. Math. Soc. Commun.	Communications de la Société Mathematique de Kharkov
Kiel. Mitth. Ver. Elbe.	Mittheilungen des Vereins nördlich der Elbe zur Verbreitung naturwissenschaftlicher Kenntnisse in Kiel
Kiel, Physiol. Inst. Arb.	Arbeiten aus dem Kieler physiologischen Institut
Kiel, Schr.	Schriften der Universität zu Kiel
Kiel Univ. Mineral. Inst. Mitth.	Mittheilungen aus dem Mineralogischen Institut der Universität Kiel
Kiev Soc. Natur. Mem.	Memoires de la Société des Naturalistes de Kiev
Kiöbenh. Bot. For.	See Bot. Tidsskr.
Kiöbenh. Bot. For. Festskr.	Festskrift, udgivet af den Botaniske Forening i Kiöbenhavn i Anledning af dens Halvhundredaars fest, den 12 April, 1890
Kiöbenh. Bot. For. Medd.	Meddelelser fra den Botaniske Forening i Kjobenhavn
Kiöbenh. Carlsb. Lab. Medd.	Meddelelser fra Carlsberg Laboratoriet
Kiöbenh. Dansk. Vid. Selsk. Afh.	Det Kongelige Danske Videnskabernes Selskabs naturvidenskabelige og mathematiske Afhandlinger

Kiöbenh., Dansk. Vid. Selsk. Skrift.	Det Kongelige Danske Videnskabernes Selskabs Skrifter. Naturvidenskabelig og Mathematisk Afdeling
Kiöbenh. Ent. For.	See Ent. Medd. (Kiobenh.)
Kiöbenh., Oversigt	Oversigt over det Kongelige Danske Videnskabernes Selskabs Forhandlinger og dets Medlemmers Arbejder i Aaret 1874(–83)...samt. med en Résumé du *Bulletin de l'Academie Royale Danoise des Sciences et des Lettres* pout l'annee 1874(–83)
Kiöbenh., Reg. Soc. Med. Acta.	Acta Regiae Societatis Medicae Havniensis.
Kiöbenh., Vidensk. Forh.	Videnskabelige Forhandlinger ved Sioelland Stifts Landemde
Kiöbenh, Vidensk. Meddel.	Videnskabelige Meddelelser fra den Naturhistoriske Forening i Kjöbenhavn
K. K. Ges. Aerzte	See Med. Jahr.
Klausenburg	See Kolozsvar
Kliniek	Kliniek
Klug, Jahr. Insect.	Jahrbücher der Insectenkunde, etc.
Koll. Chem. Beihefte	Kolloidchemische Beihefte
Kolloid-Zts.	Kolloid-Zeitschrift
Kolozsvar Orvos-Termesz. Tars. Ertes.	Ertesitö a "Kolozsvari Orvos-Termeszettudomanyi Tarsulat" -nak az ... orvosi, termeszettudomanyi szaküleseiröl ...... Proceedings of the Medical and natural history sections of the Klausenburg Medical and Natural History Society
K. Svenska Vet-Akad.	Kongl. Svenska Vetenskaps-Akademiens Handlingar
Königsb. Archiv.	Königsberger Archiv für Naturwissenschafften und Mathematik
Königsb. Med. Jahr.	Königsberger medicinische Jahrbücher; herausgegeben von dem Verein für wissenschaftliche Heilkunde zu Königsberg
Königsb. Schr.	Schriften der physikalisch-ökonomischen Gesellschaft zu Königsberg in Preussen
Kosmos (Lwow)	Kosmos. Czasopismo polskiego Towarzystwa przyrodnikow imienia Kopernika. (Cosmos. The Journal of the Polish Society Naturalists founded in honor of Copernicus)
Krain Mus.-Ver. Mitth.	See Laibach, Mus.-Ver. Krain Mitth.
Krakow Akad. (Mat.-Przyrod) Pam.	Pamietnik Akademii Umiejetnosci w Krakowie. Wydzial Matematyczno-Przyrodniczy. (Memoires of the Academy of Science in Cracow. Section of Mathematics and Natural Science)
Krakow Akad. (Mat.-Przyrod) Rozpr.	Rozprawy i Spawozdania z Posiedzen Wydzialu Matematyczno-Przyrodniczego Akademii Umiejetnosci. (Proceedings of the Section of Mathematics and Natural Science of the Academy of Science)
Krakow, Akad. (Mat.-Przyrod.) Rozpr. & Spraw.	Rozprawy i Sprawozdania z Posiedzen Wydzialu Matematyczno-Przyrodniczego Akademii Umiejetnosci. (Proceedings of the Section of Mathematics and Natural Science of the Academy of Science)
Krakow Kom. Fizyogr. Spraw.	Akademija Umiejetnosci w Krakowie. Sprawozdanie Komisyi Fizyograficznej .... (Academy of Science in Cracow. Report of the Physiographical Commission)
Krakow, Roczn. Tow. Nauk.	Rocznik Towarzystwa Naukowego z Uniwersytetem Jagiellonskim Zlaczonego
Krakau, Untersuch. Path. Anat.	Untersuchungen aus dem Pathologisch-Anatomischen Institute in Krakau

Kreutzer's Jahr. Phot.	Kreutzer's Jahresbericht der Photographie
Kristiania, Geogr. Selsk. Arb.	Det Norske Geografiske Selskabs Arbog
Kristiania, Norw. Mar. Investig. Rep.	Report on Norwegian Fishery and Marine Investigations
Kroyer, Naturhist. Tidssk.	Naturhistorisk Tidsskrift
Kühn-Archiv.	Kühn-Archiv. (formerly Berichte aus dem physiologischen Laboratorium und der Versuchsanstalt des Landwirtschaftlichen Instituts der Universität Halle
Kult. Ing.	Der Kultur-Ingenieur (F. Dünkelberg)
Kunst.	Kunstoffe
Lab. Club. Trans.	Transactions of the Laboratory Club
Laboratory	The Laboratory
Laibach, Jahr. Gymnas.	Jahresbericht des k. k. Ober-Gymnasiums in Laibach
Laibach, Jahr. Realschule	Jahresbericht der k. k. selbständigen Unter-Realschule zu Laibach
Laibach, Jahresh.	Jahresheft des Vereins des Krainischen Landes Museums in Laibach
Laibach, Mus.-Ver. Krain Mitth.	Mittheilungen des Museal-Vereins für Krain
Lancet	The Lancet, London
Landb. Cour.	Landbouw-Courant
Landshut Bot. Ver. Ber.	Bericht des Botanischen Vereines in Landshut
Landw. Centr.	Landwirthschaftliches Centralblatt für Deutschland
Landw. Jahr.	Landwirthschaftliche Jahrbücher. Zeitschrift für wissenschaftliche Landwirthschaft und Archiv. des Königlich Preussischen Landes-Oekonomie-Kollegiums
Landw. Jahr. Schweiz	Landwirtschaftliches Jahrbuch der Schweiz
Landw. Presse	Landwirtschaftliche Presse
Landw. Versuchs-Stat.	Die landwirthschaftlichen Versuchs-Stationen
Landw. Ztg.	Landwirtschaftliche Zeitung
Laon, Soc. Acad. Bull.	Bulletin de la Société Academique de Laon
Laurent Ann. Anat.	Annales Francaises et Etrangeres d'Anatomie et de Physiologie, appliquees a la Medecine et a l'Histoire Naturelle
Laurent Gerhardt, Compt. rend.	Comptes rendus Mensuels des Travaux Chemiques
Lausanne, Bull. Soc. Med.	Bulletin de la Société Medicale de la Suisse Romande
Lausanne, Bull. Soc. Vaud.	Bulletin des Seances de la Société Vaudoise des Sciences Naturelles
Lausitz. Monatschr.	Lausitzische (und neue Lausitzische) Monatschrift Organ der Oberlausitzischen Gesellschaft der Wissenschaften
Leather	Leather
Leather Mfr.	Leather Manufacturer
Leather Tr. Rev.	Leather Trades Review
Leather World	Leather World, The
Lederind.	Lederindustrie (Deutsche Gerber-Zeitung)
Ledermarkt	Ledermarkt, Der. (See also Collegium)
Leeds, Trans. Phil. Soc.	Transactions of the Philosophical and Literary Society of Leeds
Leicester, Lit. Phil Soc. Selection	Selection of Papers, of the Literary and Philosophical Society of Leicester
Leicester Soc. Rep.	Leicester Literary and Philosophical Society...Report of the Council
Leicester Soc. Trans.	Transactions of the Leicester Literary and Philosophical Society

Leide	See Leyden
Leiiden, Ann. Acad.	Annales Academiae Lugduno-Batavae
Leiden, Tijdschr. Entom.	Tijdschrift voor Entomologie
Leipzig, Abh. Jablon. Ges.	Abhandlungen bei Begründung der k. Sächsischen Gesellschaft der Wissenschaften am Tage der zweihundertjährigen Geburtsfeier Leibnizens
Leipzig, Abh. Math. Phys.	Abhandlungen der Mathematisch-Physischen Classe der Königlich Sächsischen Gesellschaft der Wissenschaften
Leipzig, Arbeit. Physiol. Anst.	Arbeiten aus der physiologischen Anstalt zu Leipzig
Leipzig, Astron. Ges. Viertelj.	Vierteljahrsschrift der Astronomischen Gesellschaft
Leipzig, Ber. Math. Phys.	Berichte über die Verhandlungen (Math. Phys. Classe) der Königlich Sächsischen Gesellschaft der Wissenschaften zu Leipzig
Leipz. Färb. Ztg.	Leipziger Färber- und Zeugdrucker-Zeitung
Leipzig Jablon. Preisschr.	Preisschriften gekrönt und herausgegeben von der fürstlich Jablonowski' schen Gesellschaft zu Leipzig
Leipzig, Monatschr. Text. Ind.	Leipziger Monatsschrift für Textil Industrie
Leipzig, Naturf. Ges. Sitzber.	Sitzungsberichte der Naturforschenden Gesellschaft zu Leipzig
Leipzig, Physiol. Anst. Arb.	Arbeiten aus der Physiologischen Anstalt zu Leipzig
Leipzig, Schr. Naturf. Ges.	Schriften der Naturforschenden Gesellschaft zu Leipzig
Leipzig, Verh. Med. Ges.	Verhandlungen der Medicinischen Gesellschaft
Leyden Mus. Notes	Notes from the Leyden Museum
Leo, Mag.	Magazin für Heilkunde und Naturwissenschaft in Pohlen
Leoben, Berg. u. Hütt. Jahr.	Berg- und Hüttenmannisches Jahrbuch der k. k. Montan. Lehranstalten zu Leoben und Pribram
Leonhard Bronn	See Neues Jahr. Mineral
Leonhard Bronn, Jahr.	Jahrbuch für Mineralogie, Geognosie, Geologie, und Petrefaktenkunde
Leonhard Bronn, Neu. Jahr.	Neues Jahrbuch für Mineralogie, Geognosie, Geologie und Petrefaktenkunde
Leonhard, Taschenbuch	Taschenbuch für die gesammte Mineralogie
Leonhard, Zts.	Zeitschrift für Mineralogie
Leopold.-Carol. Deutsch. Akad. Naturf.	See Ac. Nat. Curios. Nova Acta. Leopoldina
Leopoldina	Leopoldina. Amtliches Organ der Kaiserlichen Leopoldino-Carolinischen Deutschen Akademie der Naturforscher
Letters on Brewing	Letters on Brewing
Les Mondes	Revue hebdomadaire des Sciences et de leurs application
Licht.	Licht: Zeitschrift für Photographie: herausgegeben vom Photographischen Verein. zur Berlin
Liege, Ann. Acad.	Annales Academiae Leodiensis
Liege Assoc. Ingen. Annu.	See Rev. Univ. Mines
Liege, Mem. Soc. Emul.	Memoires de la Société Libre d'Émulation de Leiege
Liege, Mem. Soc. Sci.	Memoires de la Société (Royale) des Sciences de l'Agriculture, et des Arts a Liege
Leige Lab. Fredericq Trav.	Universite de Liege. Institut de Physiologie. Travaux du Laboratoire de Leon Fredericq
Lille Inst. Zool. Trav.	Travaux de l'Institut Zoologique de Lille et du Laboratoire de Zoologie Maritime de Wimereux (Pas-de-Calais). Travaux de la Station Zoologique de Wimereux

Lille Mem. Soc.	Memoires de la Société (Imperiale) des Sciences, de l'Agriculture et des Arts de Lille
Lille, Mem. Soc. Sci.	Memoires de la Société (Royale) des Sciences, etc., a Lille
Lille, Seances Publ.	Seances Publiques de la Société des Amateurs
Lille, Trav.	Recueil des Travaux de la Société d'Amateurs des Sciences, de l'Agriculture, et des Arts a Lille
Lille, Trav. Mem.	Travaux et Memoires de l'Universite de Lille
Lima, Mem. Cien. Nat.	Memorias de Ciencias Naturales y de Industrial (Lima)
Limbourg, Soc. Sci. Bull.	Bulletin de la Société Scientifique et Litteraire du Limbourg
Limoges, Assises	Assises scientifiques de Limoges (Institut des Provices de France)
Lindblom, Bot. Notiser	Botaniska Notiser
Linn	Linnaea: ein Journal für die Botanik
Linn Entom.	Linnaea Entomologica
Linn. Soc. J.	The Journal of the Linnean Society. Botany and Zoology
Linn. Soc. Trans.	The Transactions of the Linnean Society of London
Linn. Soc. Proc.	Proceedings of the Linnean Society of London
Linneska Samf. Handl.	Linneska Samfundets Handlingar for ar 1832
Linz, Ber.	Bericht über das Museum Francisco-Carolinum in Linz
Lisboa, Acad. Sci. Mem.	Historia e Memorias da Academia Real das Sciencias de Lisboa
Lisboa, Actas	Actas das Sessoes da Academia Real das Sciencias de Lisboa
Lisboa, Ann.	Annaes das Sciencias e Lettras
Lisboa, J. Math. Sci.	Jornal de Sciencias Mathematicas, Physicas e Naturaes publicado sob os Auspicios da Academia Real das Sciencias de Lisboa
Litterar. Annal.	Litterarische Annalen der gesammten Heilkunde
Liverpool Biol. Soc. Proc.	Proceedings and Transactions of the Liverpool Biological Society
Liverpool, Lit. Phil. Soc. Proc.	Proceedings of the Literary and Philosophical Society of Liverpool
Liverpool Mar. Biol. Comm.	See Liverpool Biol. Soc. Proc.; Liverpool Biol. Soc. Proc. & Trans.; Liverpool Lit. Phil. Soc. Proc.
Liverpool Med. Chir. J.	Liverpool Medico-Chirurgical Journal
Liverpool School Trop. Med. Mem.	Liverpool School of Tropical Medicine. Memoirs
Liverpool, Thompson Yates Lab. Rep.	The Thompson Yates Laboratories Report
Loc. Gov. Bd. Rep. (Med. Off.)	...Annual Report of the Local Government Board. Supplement containing the Reports of the Medical Officer
London	See Int. Congr. Hyg. Trans., 1891; Int. Congr. Zool. Proc. 1898
London, Ann. Med. Surg.	Annals of Medicine and Surgery, Records of the occurring Improvements, &c.
London, Cryst. Soc. Proc.	Proceedings of the Crystallological Society
London Elec. Soc. Proc.	Proceedings of the London Electrical Society
London, Fed. Inst. Brewing J.	Journal of the Federated Institutes of Brewing containing the Transactions of the various Institutes
London J. Med.	London Journal of Medicine
London, Med. Phys. J.	The Medical and Physical Journal
London, Med. Soc. Trans.	Transactions of the Medical Society of London

London, Obstet. Soc. Trans.	Transactions of the Obstetrical Society of London
London, Odont. Soc. Trans.	Transactions of the Odontological Society of London
London Path. Soc. Trans.	Transactions of the Pathological Society of London
Lond. Phot. Soc.	London Photographic Society
London Phys. Soc. Proc.	Proceedings of the Physical Society of London
London Physiol. J.	London Physiological Journal
London Poly. Rev.	The London Polytechnic Review and Magazine
London, Poly. Mag.	Polytechnic Magazine and Journal of Science, Letters, and Fine Arts
London, Sci. Soc. Proc.	Proceedings of the Scientific Society of London
London, Soc. Imp. Med. Trans.	Transactions of the Society for the Improvement of Medical and Chirugical Knowledge
Lotos	Lotos, Jahrbuch für Naturwissenschaft im Auftrage der Vereines "Lotos"
Lousiana Planter	Louisiana Planter and Sugar Maufacturer, The
Louvaine, Ann. Acad.	Annales Academiae Lovaniensis
Lowell Obs. Ann.	Annals of the Lowell Observatory
Lucca, Atti Accad.	Atti della R. Accademia Lucchese di Scienze, Lettere, et Arti
Lumière	La Lumière; Revue de la Photographie
Lumière elec.	Lumière electrique, La
Lund, Acta Univ.	Acta Universitatis Lundensis. Lunds Iniversitets Ars-skrift. Afdelningen för Mathematik och Naturvetenskap
Lund Bot. För.	See Bot. Centrbl.; Bot. Notiser
Lund, Phys. Sällsk. Tidskr.	Physiografiska Sällskapets Tidskrift
Lüneb., Denkschr.	Denkschriften des naturwissenschaftlichen Vereins für das Füsrtenthum Lüneburg
Lüneb., Jahr. Naturwiss. Ver.	Jahresbericht über die Thätigkeit des naturwissenschaftlichen Vereins in Lüneburg
Lüneb. Jheft. Naturwiss. Ver.	Jahreshefte des Naturwissenschaftlichen Vereins für das Fürstentum Lüneburg
Luxemb., Inst. Roy. Publ.	Publications de l'Institut Royal Grand-Ducal de Luxembourg: Section des Sciences Naturelles
Luxemb. P.	Luxembourg Patent
Luxemb. Soc. Bot. Rec. Mem. Trav.	Recueil des Memoires et des Travaux publies par la Société Botanique du Grant-Duche de Luxembourg
Luxemb. Soc. Sci. Natur.	Société des Sciences Naturelles du Grand-Duche de Luxembourg
Lyon	Lyon scientifique et industriel
Lyon, Acad. Sci. Mem.	Memoires de l'Academie des Sciences, Belles-Lettres, et Arts de Lyon
Lyon Mus. Hist. Natur. Archiv.	Archives du Museum d'Histoire naturelle de Lyon
Lyon Soc. Agric. Ann.	Annales de la Société d'Agriculture, Histoire naturelle et Arts utiles de Lyon. Annales de la Société d'Agriculture, Sciences et Industrie de Lyon
Lyon Soc. Bot. Ann.	Annales de la Société Botanique de Lyon
Lyon, Soc. Linn. Ann.	Annales de Socétié Linneenne de la Lyon
Lyon, Soc. Linn. Compt. rend.	Comptes Rendus des Travaux de la Société de Medecine
Lyon, Soc. Sci. Med. Mem.	Memoires et Comptes-Rendus de la Société des Sciences Medicales de Lyon
Lyon Univ. Ann.	Annales de l'Universite de Lyon
Maandbl. Natuurweten.	Maandblad voor Natuurwetenschappen, uitgegeven door de Sectie voor Natuurwetenschappen van het Gennotschap ter Bevordering van Natuur-, Genees- en Heelkunde te Amsterdam

Maclurian Lyceum, Contrib.	Contributions of the Maclurian Lyceum to the Arts and Sciences
Macon Acad. Ann.	Annales de l'Academie de Macon. Société des Arts, Sciences, Belles-Lettres et (d')Agriculture (de Saone-et-Loire)
Macon, Soc. Agric. Compt. rend.	Comptes Rendus des Travaux de la Société d'Agriculture, Sciences, et Belles-Lettres
Macon Soc. Compt. rend.	Compte Rendu des Travaux de la Société (d'Agriculture), des Sciences, Arts et Belles-lettres, de Macon
Madras J.	The Madras Journal of Literature and Science
Madras Quart. J.	Madras Quarterly Journal of Medical Science
Madrid	See Congr. Int. Hig. Act. 1898
Madrid Acad. Cien. Mem.	Memoires de la Real Academia de Ciencias Exactas, Fisicas y Naturales de Madrid
Madrid, Anales Hist. Natur.	Anales de Historia Natural
Madrid, Anales Minas	Anales de Minas
Madrid, Anuar.	Anuario del Real Observatorio de Madrid
Madrid, Bol.	Boletin Oficial del Ministerio de Comercio
Madrid, Ingen. Ind. Anales	Anales de la Asociacion de Ingenieros Industriales
Madrid, Mem.	Memorias de la Real Academia de Ciencias
Madrid, Revista	Revista de los Progresos de las Ciencias exactas, fisicas, y naturales
Madrid, Soc. Hist. Natur. Anales	Anales de la Sociedad Espanola de Historia Natural
Mag. Gesammt. Thierheilk.	Magazin für die gesammte Thierheilkunde
Mag. Natur. Hist.	The Magazine of Natural History, and Journal of Zoology, Botany, Mineralogy, Geology, and Meteorology
Mag. Natur. Phil.	The Magazine of Natural Philosophy
Mag. Naturvid.	Magazin for Naturvidenskaberne
Mag. Zool.	Magasin de Zoologie
Magdeb. V. Ver. Abh. Naturwiss.	Abhandlungen des Naturwissenschaftlichen Vereins zu Magdeburg
Magdeb. V. Ver. Festschr. Naturwiss.	Festschrift zur Feier des 25 jährigen Stiftungstages des Naturwissenschaftlichen Vereins zu Magdeburg
Magdeb. V. Ver. Jahr. Abh. Naturwiss.	Jahresbericht und Abhandlungen des naturwissenshaftlichen Vereins in Magdeburg.
Magendie, J. Physiol.	Journal de Physiologie, experimentale et pathologique
Magyar Akad. Ertes. (Math. Termesz.)	Magyar Akademiai Ertesitö. A mathematikai, es Termeszettudomanyi osztalyok közlönye. (Report of the Hungarian Academy. Communications of the Mathematical and Natural Science Sections)
Magyar Böripar	Magyar Böripar
Magyar Nemzeti Muzeum	See Termr. Füz.
Magyar Termt. Tars.	See Termt. Közlön.
Magyar Tud. Akad. Ertes.	A Magyar Tudomanyos Akademia Ertesitoje. (Report of the Hungarian Academy of Science) Akademiai Ertesito a Magyar Tud. Akademia Megbizasabol. (Report by the Committee of the Hungarian Academy of Science)
Magyar Tud. Akad. Ertek. (Math.)	Ertekezesek a Mathematikai Tudomanyok köreböl. Kiadja a Magyar Tudomanyos Akademia. (Memoirs in the Mathematical Sciences. Published by the Hungarian Academy of Science)

Magyar Tud. Akad. Ertek. (Termt.)	Ertekezesek a Termeszettudomanyok körebol. Kiadja a Magyar Tudomanyos Akademia. (Memoirs in the Natural Sciences. Published by the Hungarian Academy of Science)
Magyar Tud. Akad. Evk.	A Magyar Tudomanyos Akademia Evkönyvei. (Annals of the Hungarian Academy of Science)
Maine Loire Soc. Mem. Acad.	Memoires de la Société Academique de Maine et Loire
Majocchi, Ann. Fis. Chim.	Annali di Fisica, Chimica, etc.
Malpighia	Malpighia. Rassegna mensuale di Botanica
Malta P.	Malta Patent
Malvern Field Club Trans.	The Transactions of the Malvern Naturalists' Club
Manufact. and Build.	The Manufacturer and Builder
Manchester, Engin. Proc.	Proceedings of the Manchester Institution of Engineers
Manchester, Lit. Phil. Soc. Mem.	Memoirs of the Literary and Philosophical Society of Manchester
Manchester, Lit. Phil. Soc. Proc.	Proceedings of the Literary and Philosophical Society of Manchester
Manchester Micro. Soc. Trans.	Manchester Microscopical Society. Transactions and Annual Report
Manchester, Owens Coll. Biol. Lab. Stud.	Studies from the Biological Laboratories of the Owens College
Manchester, Owens Coll. Stud. Biol.	Studies in Biology from the Biological Department of the Owens College
Mannheim, Jahr.	Jahresbericht des Mannheimer Vereins für Naturkunde
Mans, Soc. Agric. Bull.	Bulletin de la Société d'Agriculture, etc., de la Sarthe
Mans, Soc. Bull.	Bulletin de la Société (Royale) d'Agriculture, Sciences et Arts du Mans
Mans, Soc. Roy. Trav.	Analyse des Travaux de la Société (Royale) des Arts du Mans
Marburg, Ges. Naturwiss. Schr.	Schriften der Gesellschaft zur Beförderung der gesammten Naturwissenschaften zu Marburg
Marianini	See Mem. Fis. Sperim.
Marne, Soc. Agric. Compte Annuel	Compte annuel et Sommaire des Travaux de la Société Agricole, etc., du departement de la Marne
Marne, Soc. Agric. Seance	Seance publique de la Société d'Agriculture, etc., du departement de la Marne
Marseille, Ann. Sci.	Annales de Sciences et de l'Industrie du midi de la France
Marseille Fac. Sci. Ann.	Annales de la Faculte des Sciences de Marseille
Marseille Lab. Zool. Mar. Trav.	See Marseille Mus. Ann.
Marseille, Mem. Acad.	Memoires publies par l'Academie de Marseille
Marseille, Mem. Soc. Emul.	Memoires de la Société d'Émulation de la Provence
Marseille Mus. Ann.	Annales du Musee d'Histoire naturelle de Marseille
Maschin.-Constr.	Der praktische Maschinen-Construkteur (W. Uhland)
Maschinenb.	Der Maschinenbauer
Mass. Bd. Health Report	Annual Report of the State Board of Health, Lunacy and Charity of Massachusetts. Annual Report of the State Board of Health of Massachusetts
Mass. Insects Report	...Annual Report on the Injurious and Beneficial Insects of Massachusetts
Mass. Med. Soc. Commun.	Massachusetts Medical Society's Communications
Mat. grasses	Le Matieres grasses
Maurice, Soc. Hist. Natur. Rapp.	Septieme Rapport Annuel sur les Travaux de la Société d'Histoire Naturelle de l'Lle Maurice

Mauritius, Meteorol. Soc. Proc.	Proceedings, &c., of the Meteorological Society of Mauritius
Mauritius, Meteorol. Soc. Trans.	Transactions of the Meteorological Society of Mauritius
Mauritius P.	Mauritius Patent
Mauritius Roy. Soc. Trans.	Transactions de la Société Royale des Arts et des Sciences de Maurice
Meaux, Bull. Soc. Archeol.	Bulletin de la Société d'Archeologie, Sciences, Lettres et Arts du dept. de Seine et Marne
Mechan. Engin. Inst. Proc.	Institution of Mechanical Engineers. Proceedings
Meckel, Archiv.	Archiv. für Anatomie und Physiologie
Meckel, Deut. Archiv.	Deutsches Archiv. für die Physiologie
Med. Assoc. J.	Journal edited for the Provincial Medical and Surgical Association
Med. Bot. Soc. Trans.	Transactions of the Medico-Botanical Society of London
Med. Chem. Unters.	Medicinish-chemische Untersuchungen; aus dem Laboratorium für angewandte Chemie zu Tübingen
Med. Chir. Soc. Proc.	Proceedings of the Royal Medical and Chirurgical Society of London
Med.-Chir. Trans.	Medico-Chirurgical Transactions
Med. Chir. Ztg.	Medicinisch-chirurgische Zeitung
Med. Congr.	See Congr. Int. Med. C. R., Congr. Int. Sci. Med. C. T., Congr. Med. Int. Atti., Int. Med. Congr. Trans., Int. Med. Congr. Verh.
Med. Jahr.	Medizinische Jahrbücher, von der K. K. Gessellschaft in Wien
Med. Klinik.	Medizinische Klinik
Med. naturwiss. Archiv.	Medizinisch-naturwissenschaftliches Archiv.
Med. Off. India Sci. Mem.	Scientific Memoirs by Medical Officers of the Army of India
Med. Phys. J.	The Medical and Physical Journal
Med. Rec.	The Medical Record, N. Y.
Med. Times	The Medical Times, London
Med. Trans.	Medical Transactions
Med. Wochenschr.	Medizinische Wochenschrift
Med. Ztg. Russ.	Medicinische Zeitung Russlands
Medd. Gronland	Meddelelser om Gronland
Medd. K. Vetenskapsakad. Nobel-inst.	Meddelanden frän K. Vetenskapsakademiens Nobelinstitut
Meisner, Ann.	Annalen der allgemeinen Schweizerischen Gesellschaft für die gesammten Naturwissenschaften
Meisner, Anzeiger	Naturwissenschaftlicher Anzeiger der Allgemeinen Schweizerischen Gesellschaft für die gesammten Naturwissenschaften
Melbourne	See Victoria
Mem. accad. Lincei	Memorie della r. accademia dei Lincei, Classe di scienze fisiche, mathematiche e naturali
Mem. Accad. Sci. Torino	Memorie della Reale Accademia delle Scienze di Torino
Mem. Chem. Soc.	Memoirs and proceedings of the Chemical Society of London prior to 1848
Mem. Coll. Sci. Eng. Kyoto	Memoirs of the College of Science and Engineering, Kyoto Imperial University
Mem. Fis. Sperim.	Memorie di Fisica sperimental
Mem. Imp. Mineral. Soc. Petrograd	Memoirs of the Imperial Mineralogical Society of Petrograd
Mem. Lepidopt., St. Petersb.	Memoires sur les Lepidopteres

Mem. Manch. Lit. Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society
Mem. Med. Milit.	Recueil de Memoires de Medecine, de Chirurgie et de Pharmacie Militaires
Mem. poud. salp.	Memorial des poudres et salpetres
Mem. rev. soc. cien. "Antonio Alzate"	Memorias y revista de la sociedad cientifica "Antonio Alzate"
Mem. Soc. Ing. civ.	Memoires et Compte-Rendu des travaux de la Société des Ingenieurs Civils, etc.
Mem. Soc. Nat. Kiev.	Memoirs of the Society Nat. Kiev.
Mem. Valdarnesi	Memorie Valdarnesi
Mende, Soc. Agric. Bull.	Bulletin de la Société d'Agriculture, Industrie, Sciences, et Arts de departement de la Lozere
Mende, Soc. Agric. Mem.	Memoires et Analyses des Travaux de la Société d'Agriculture, Commerce, Sciences, et Arts de la ville de Mende, departement de la Lozere
Merck's Ann. Rep.	Merck's Annual Report
Merck's Archiv.	Merck's Archives, New York
Messenger Math.	The Messenger of Mathematics
Met.	Metallurgical-Metallurgia
Met. Chem. Eng.	Metallurgical and Chemical Engineering
Met. ital.	Metallurgia italiana, La
Met. Rev.	The Metallurgical Review
Metal Ind.	The Metal Industry
Metal Tech.	Metal Technik
Metall. Ind. Ztg.	Deutsche Metall-Industrie-Zeitung
Metallarb.	Der Metallarbeiter
Metallurgie	Metallurgie
Metaxa, Ann. Med. Chir.	Annali medico-chirurgici.
Metz Acad. Mem.	Memoires de l'Academie (Imperiale) de Metz
Metz, Assises	Assises scientifiques de Metz (Institut des Provinces de France)
Metz, Seance Gen.	Société des Lettres, Sciences, Arts, et Agriculture de Metz
Metz Soc. Hist. Natur. Bull.	Bulletin de la Société d'Histoire naturelle de Metz
Mex.	Mexican, Mexico, Mexicane
Mex. P.	Mexican Patent
Mex. Mus. Anales	Anales del Museo Nacional de Mexico
Mex. Registro Trim.	Registro trimestre, o Coleccion de Memorias de Historia, Literatura, Ciencias, etc., por una Sociedad de Literatos
Mex. Soc. "Alzate" Mem.	Memorias de la Sociedad Cientifica "Antonio Alzate"
Mexique Archiv. Comm. Sci.	Archives de la Commission Scientifique du Mexique, publiees sous les auspices du Ministere de l'Instruction Publique
Meyer Bros. Drug.	Meyer Brothers Druggist, St. Louis
Meyer Jahr. Chem.	R. Meyer's Jahrbuch der Chemie
Michigan, Fish Comm. Report	Biennial Report of the State Board of Fish Commissioners. (Contains the Michigan Fish Comm. Bull.)
Micro. J.	Quarterly Journal of Microscopical Science
Micro. Soc. J.	Journal of the Royal Microscopical Society
Micro. Soc. Trans.	Transactions of the Microscopical Society of London
Midl. Drug.	Midland Druggist and Pharmaceutical Review
Midl. Med. Surg. Rep.	Midland Medical and Surgical Reporter
Midl. Quart. J. Med. Sci.	The Midland Quarterly Journal of Medical Sciences
Milano, Ann. Scienz.	Annali di Scienze e Lettere

Milano, Atti Ginnas.	Atti dell' I. R. Ginnasio Liceale Convitto Longone in Milano
Milano, Atti Ist. Lomb.	Atti dell' I. R. Istituto Lombardo di Scienze, Lettere, ed Arti
Milano, Atti Soc. Ital.	Atti della Societa Italiana di Scienze Naturali
Milano, Cagnola Atti	Atti della Fondazione Scientifica Cagnola dalla sua istituzione in poi.
Milano, Giorn. Soc. Incor.	Giornale della Societa d'Incorragiamento delle Scienze, etc., stabilita in Milano
Milano, Ist. Lomb. Adunanze	Solenni Adunanze del R. Istituto Lombardo di Scienze e Lettere
Milano, Ist. Lomb. Rapporti	Rapporti sui Progressi delle Scienze del R. Istituto Lombardo di Scienze
Milano, Ist. Lomb. Rend.	Rendiconti dell' Istituto Lombardo di Scienze e Lettere:—Classe di Scienze matematiche e naturali
Milano, Mem. Ist. Lomb.	Memorie dell' I. R. Istituto Lombardo di Scienze, etc.
Milano, Mem. Ist. Lomb. Veneto	Memorie dell' I. R. Istituto del regno Lombardo-Veneto
Milch. Zentr.	Milchwirtschaftliches Zentralblatt
Milch Ztg.	Milch Zeitung
Min. Eng. World	Mining and Engineering World
Min. J.	The Mining Journal
Min. Rev.	Mining Review, a Monthly Record of Geology
Min. Sci.	Mining Science
Min. Sci. Press	Mining and Scientific Press
Min. Smelt. Mag.	The Mining and Smelting Magazine: a monthly review of Practical Mining, Quarrying, and Metallurgy
Min. Soc. J.	See Min. Mag.
Mineral. Mag.	The Mineralogical Magazine and Journal of the Mineralogical Society of Great Britain and Ireland
Mineral. Mitth.	Mineralogische Mittheilungen
Mineral. Petr. Mitth.	(Tschermak's) Mineralogische und Petrographische Mittheilungen
Mines and Minerals	Mines and Minerals
Minn. Acad. Sci. Bull.	Bulletins of the Minnesota Academy of Natural Sciences
Minn. Acad. Sci. Pap.	The Minnesota Academy of Natural Sciences at Minneapolis, Minn. Occasional Papers
Minn. Bot. Stud.	Geological and Natural History Survey of Minnesota. Minnesota Botanical Studies
Miquel, Bull.	Bulletin des Sciences Physiques et Naturelles en Neerlande
Misc. Ent.	Miscellanea Entomologica
Mitau, Quatember	Die Quatember
Mitth. Artil. Geniew.	Mittheilungen über Gegenstände des Artillerie- und Genie-wesens
Mitth. Böhmen. Archit. Ing. Ver.	Mittheilungen des Architekten und Ingenieur Vereins im Königreiche Böhmen
Mitth. Centralst. Wiss.-tech. Unters.	Mittheilungen aus der Centralstelle für wissenschaftlichtechnische Untersuchungen
Mitth. Gewerbever. Nassau	Mittheilungen für den Gewerbeverin für Nassau
Mitth. Kais. Gesundhts.	Mittheilungen aus dem Kaiserlichen Gesundheitsamte, Berlin
Mitth. Königl. Materialprüfungsamt	Mitteilungen aus dem Königlichen Material prüfungsamt zu Gross Lichterfelde West
Mitth. Hannov. Gewerbever.	Mittheilungen des Gewerbevereins für Hannover

Mitth. Lebensm. Hyg.	Mitteilungen aus dem Gebiete der Lebensmitteluntersuchung und Hygiene veröffentlicht vom Schweizer Gesundheitsamt
Mitth. Malerei	Technische Mitteilungen für Malerei
Mitth. könig... Prüfungsans. Wasser-versorgung	Mitteilungen aus der königlichen Prüfungsanstalt für Wasser-versorgung und Abwässer beseitung zu Berlin
Mitth. Tech. Gew. Mus.	Mitteilungen aus dem Technischen Gewerbe Museum
Mitth. Techn. Versuchsamtes	Mittheilungen des k. k. Technischen Versuchsamtes
Mitth. Zool. Sta. Neapel	Mittheilungen aus der zoologischen Station zu Neapel, etc.
Mo. Insects Report	Annual Report on the Noxious, Beneficial and other Insects, of the State of Missouri, made to the State Board of Agriculture
Mod. Sugar Planter	Model Sugar Planter, The
Modena, Accad. Sci. Mem.	Memorie della Regia Accademia di Scienze, Lettere ed Arti di Modena
Modena, Annu. Soc. Natur.	Annuario della Societa dei Naturalisti in Modena
Modena Atti Soc. Natur.	Atti della Societa dei Naturalisti di Modena
Modena, Mem. Soc. Ital.	Memorie di Matematica e di Fisica della Societa Italiana delle Scienze
Modena, Relazione	Relazione delle Adunanze della R. Accademia di Scienze, Lettere, ed Arti di Modena, nell' Anno Academico 1842–43
Moigno, Annu. Cosmos	Annuaire du Cosmos
Mois chim. electrochim.	Mois chimique et electrochimique, Le
Mois min. met.	Mois minier et metallurgique, Le
Mois sci. ind.	Mois scientifique et industriel, Le
Moleschott, Unters.	Untersuchungen zur Naturlehre des Menschen und der Thiere
Moll, Ann.	Annalen der Berg- und Hüttenkunde
Moll, Efemeriden	Efemeriden der Berg- und Hüttenkünde
Moll, Jahr. Berg.	Jahrbücher der Berg- und Hüttenkunde
Moll, Neue Jahr.	Neue Jahrbücher der Berg- und Hüttenkunde
Mon. ceram. verr.	Moniteur de la ceramique de la verrerie et journal du ceramiste et du chaufournier (reuins)
Mon. cord.	Moniteur de la cordonnerie
Mon. fils. tiss.	Moniteur des fils et tissus
Mon. Ind.	Moniteur Industriel
Mon. Ind. Belge	Moniteur Industriel Belge
Mon. Pap.	Moniteur Papeterie
Mon. Sci.	Moniteur Scientifique (Quesneville)
Mon. teint.	Moniteur de la teinture des apprets et de l'impression des tissus
Monats.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften. Gesammelte Abbhandlungen aus den Sitzungsberichten der kaiserlichen Akademie der Wissenschaften
Monats. Dermatol.	Monatshefte für praktische Dermatologie
Monatsbl. Hannover Gewerbever.	Monatsblatt des Gewerbevereins für Hanover
Monatschr. Text.-Ind.	Leipziger Monatsschrift für Textil-Industrie
Monatschr. Zahn.	Monatschrift für Zahnärzte
Montevideo Mus. Nac. Anales	Anales del Museo Nacional de Montevideo
Monthly Amer. J. Geol.	The monthly Journal of Geology and Natural Science
Monthly Archiv. Med. Sci.	Monthly Archives of the Medical Sciences

Monthly Cons. & Trade Report	The monthly Consular and Trade Reports
Montpellier, Acad. Proces-Verb.	Extraits des Proces-Verbaux des Seances de l'Academie des Sciences et Lettres
Montpellier, Acad. Sci. Mem.	Academie des Sciences et Lettres de Montpellier
Montpellier Inst. Zool. Trav.	Travaux originaux du Laboratoire Zoolique de la Faculte des Sciences de Montpellier et de la Station Maritime de Cette
Montpellier, Mem. Acad. Sect. Med.	Memoires de l'Academie des Sciences et Lettres: Section de la Medecine
Montpellier, Recueil. Bull.	Recueil des Bulletins publies par la Société Libre des Sciences, etc.
Montreal Natur. Hist. Soc. Proc.	See Canad. Rec. Sci.
Montreal Pharm. J.	Montreal Pharmaceutical Journal
Montsouris	See under Paris
Morphol. Arb.	Morphologische Arbeiten
Morphol. Jahr.	Morphologisches Jahrbuch
Moscou	See Congr. Int. Anthrop. C. R. 1892, Congr. Int. Med. C. R. 1897, Congr. Int. Zool. (C. R.) 1892
Moscou, Comment. Soc. Phys. Med.	Commentationes Societatis Physico-Medicae apud Universitatem Mosquensem institutae
Moscou, Soc. Natur. Bull.	Bulletin de la Société Imperiale des Naturalistes
Moscou, Soc. Natur. Mem.	Memoires de la Société Imperiale des Naturalistes de Moscou
Moscou, Soc. Natur. Nouv. Mem.	Nouveaux Memoires de la Société Imperiale des Naturalistes de Moscou
Moscow Soc. Sci. Bull.	Bulletin of the Imperial Society of Lovers of Natural Science, Anthropology and Ethnography, in connection with the Imperial University of Moscow
Moscow Univ. Mem. (Natur. Hist.)	Scientific Memoirs of the Imperial University of Moscow. . Natural History Section
Moscow Univ. Mem. (Phys.-Math.)	Scientific Memoirs of the Imperial University of Moscow. Physico-Mathematical Section
Moselle, Bull. Soc. Hist. Natur.	Bulletin de la Société d'Histoire Naturelle du departement de la Moselle
Moselle, Trav. Soc. Sci. Med.	Expose des Travaux de la Société des Sciences Medicales de la Moselle
Mov. Pict. World	Moving Picture World
Mulder, Archief.	Natuur- en Scheikundig Archief.
Mulder, Scheik. Verh.	Scheikundige Verhandelingen en Onderzoekingen
Müller, Archiv.	Archiv. für Anatomie, Physiologie, und wissenschaftliche Medicin.
München, Akad. Abh.	Abhandlungen der Mathematisch-Physikalisch Classe der königlich Bayerischen Akademie der Wissenschaften
München, Akad. Sitzber.	Sitzungsberichte der Mathematisch-Physikalischen Classe der k. B. Akademie der Wissenschaften München
München Bot. Ver.	See Bot. Centrbl.
München, Bull. Akad.	Bulletin der k. Akademie der Wissenschaften
München, Denkschr.	Denkschriften der Königl. Baierischen Akademie der Wissenschaften zu München
München, Entom. Ver. Mitth.	Mittheilungen des Münchener Entomologischen Vereins
München, Gelehrte Anz.	Gelehrte Anzeigen

München Ges. Morphol. Physiol. Sitzber.	Sitzungsberichte der Gesellschaft für Morphologie und Physiologie in München
München, Naturwiss. Tech. Comm. Abh.	Abhandlungen der naturwissenschaftlichtechnischen Commission bei der Königl. Baierischen Akademie
München Phot. Ges.	See Wien, Photogr. Correspond.
München, Sitzber.	Sitzungsberichte der Königl. Baierischen Akademie der Wissenschaften zu München
München Thierarznei-Schule Jahr.	Jahresbericht der k. Central-Thierarznei-Schule in München
München Thierärztl. Hochschule Jahr.	Jahresbericht der k. Thierärztlichen Hochschule in München
München, Zts. Archit.	Zeitschrift des Bayerischen Architekten- und Ingenieur-Vereins
Munic. Engin.	Municipal Engineer
Munic. J. Engin.	Municipal Journal and Engineer
Münster, Abh. Aerzt. Ges.	Abhandlungen und Beobachtungen der ärztlichen Gesellschaft zu Münster
Museum Senckenb.	Museum Senckenbergianum
Must. Ztg.	Leipziger Färber Zeitung (Färberei Musterzeitung)
N. Brunsw. Natur. Hist. Soc. Bull.	Bulletin of the Natural History Society of New Brunswick
N. England Bot. Club	See Rhodora
N. Engl. Eng.	New England Engineer, The
N. England J. Med.	New England Journal of Medicine and Surgery.
N. Erf. Erfahr.	Neuste Erfindungen und Erfahrungen
N. Hampshire San. Bull.	New Hampshire Sanitary Bulletin
N. Haven	See Connecticut
N. Idea	New Idea (The), Detroit
N. Med. Phys. J.	New Medical and Physical Journal
N. Mex. Agric. Coll. Bull.	New Mexico Agricultural College. Experiment Station. Las Crues, N. M. Bulletin. New Mexico College of Agriculture and the Mechanic Arts. Agricultural Experimental Station Bulletin
N. Orleans Med. Surg. J.	New Orleans Medical and Surgical Journal
N. Orleans Proc.	Proceedings of the New Orleans Academy of Sciences
N. Russ. Soc. Natur. Mem.	Memoirs of the New Russian Society of Naturalists
N. S. Wales, Acclim. Soc. Report	Annual Reports (3, 6, and 7) of the Acclimatisation Society of N. S. W.
N. S. Wales Dept. Mines Report	Annual Report of the Department of Mines (and Agriculture), New South Wales
N. S. Wales, Entom. Soc. Trans.	The Transactions of the Entomological Society of New South Wales
N. S. Wales Linn. Soc. (Macleay Mem. Vol.)	Linnean Society of New South Wales. The Macleay Memorial Volume
N. S. Wales, Linn. Soc. Proc.	The Proceedings of the Linnean Society of New South Wales
N. S. Wales P.	New South Wales Patent
N. S. Wales, Phil. Soc. Trans.	Transactions of the Philosophical Society of New South Wales
N. S. Wales, Roy. Soc. J.	Journal and Proceedings of the Royal Society of New South Wales
N. S. Wales, Roy. Soc. Trans.	Transactions of the Royal Society of New South Wales
N. Y. Acad. Ann.	Annals of the New York Academy of Sciences, late Lyceum of Natural History
N. Y. Acad. Mem.	New York Academy of Sciences. Memoirs
N. Y. Acad. Trans.	Transactions of the New York Academy of Sciences. Late Lyceum of Natural History

N. Y. Acad. Med. Bull.	Bulletin of the New York Academy of Medicine
N. Y. Acad. Med. Trans.	Transactions of the New York Academy of Medicine
N. Y. Agric. Soc. Trans.	Transactions of the New York State Agricultural Society
N. Y. Bot. Club Bull.	Bulletin of the Torrey Botanical Club
N. Y. Entom. Soc. J.	Journal of the New York Entomological Society
N. Y. Insects Report	Report on the Noxious, Beneficial and other Insects of the State of New York
N. Y. J. Med.	New York Journal of Medicine and the Collateral Sciences
N. Y. Linn. Soc. Trans.	Transactions of the Linnaean Society of New York
N. Y. Lit. Phil. Soc. Trans.	Transactions of the Literary and Philosophical Society of New York
N. Y. Lyceum Ann.	Annals of the Lyceum of Natural History of New York
N. Y. Lyceum, Proc.	Proceedings of the Lyceum of Natural History in the City of New York
N. Y. Med. J.	New York Medical Journal
N. Y. Med. Repos.	Medical Repository of New York
N. Y. Med. Soc. Trans.	Transactions of the Medical Society of the State of New York
N. Y. Mus. Bull.	University of the State of New York. Bulletin of the New York State Museum
N. Y. Mus. Mem.	Memoirs of the New York State Museum
N. Zeal. Inst. Trans.	Transactions and Proceedings of the New Zealand Institute
N. Zeal. Inst. Min. Engin. Trans.	Transactions of the New Zealand Institute of Mining Engineers
N. Zeal. J. Sci.	The New Zealand Journal of Science
N. Zeal. P.	New Zealand Patent
N. Zeal. Pap. & Rep.	New Zealand. Papers and Reports relating to Minerals and Mining
Nachr. königl. Ges.	Nachrichten von der königlichen Gesellschaft der Wissenschaften zu Göttingen. (Mathematische-physikalische Klasse)
Nancy, Acad. Stanislas. Mem.	Academie de Stanislas. Memoires de la Société (Royale) des Sciences, etc., de Nancy
Nancy Soc. Sci. Bull.	Bulletin de la Société des Sciences de Nancy
Nancy Soc. Sci. Mem.	Memoires de la Société (Royale) des Sciences, Lettres, et Arts de Nancy
Nancy Soc. Sci. Trav.	Precis analytique des Travaux de la Société (Royale) des Sciences, Arts, et Agriculture de Nancy
Nantes J. Med.	Journal de la Section de Medecine de la Société Academique du departement de la Loire Inferieure
Nantes, Ann. Soc. Acad.	Annales de la Société Academique de Nantes et du departement de la Loire Inferieure
Nantes Soc. Sci. Natur. Bull.	Bulletin de la Société des Sciences naturelles de l'Ouest de la France
Napoli Accad. Aspir. Ann.	Annali della Accademia degli aspiranti Naturalisti
Napoli Accad. Atti	Atti della Reale Accademia delle Scienze Fisiche e Matematiche
Napoli Accad. Pontan. Atti	Atti dell' Accademia Pontaniana
Napoli Accad. Sci. Atti	Atti della Reale Accademia della Scienze e Belle Lettere; Sezione della Societa R. Borbonica
Napoli Accad. Sci. Mem.	Memorie della R. Accademia della Scienze
Napoli Giorn. Mat.	See Giornale di Matemat.
Napoli, Atti Ist. Incorr.	Atti del Real Istituto d'Incorraggiamento alle Scienze Naturali di Napoli

Napoli Lucifero	Il Lucifero
Napoli Mus.	Museo di Letteratura e Filosofia
Napoli, Ann. Mus. Zool.	Annuario del Museo Zoologico della R. Universita di Napoli
Napoli Rend.	Rendiconto dell' Accademia delle Scienze Fisiche e Matematiche. (Sezione della Societa Reale di Napoli)
Napoli Soc. Natur. Boll.	Bollettino della Societa di Naturalisti in Napoli
Natl. Assoc. Retail Drug, Notes	The Journal of the National Association of Retail Druggists, Chicago
Natl. Disp.	National Dispensatory
Natl. Drug.	National Druggist
Natl. Eclect. Med. Assoc. Quart.	The National Eclectic Medical Association Quarterly, Cincinnati
Natl. Glass Budget	National Glass Budget
Natl. Inst. Bull.	Bulletin of the Proceedings of the National Institution for the Promotion of Science
Natur. Can.	Le Naturaliste Canadien. Bulletin de Recherches, Observations et Decouvertes se rapportant a l'Histoire naturelle du Canada
Natur. Sicil.	Il Naturalista Siciliano. Giornale di Scienze Naturali
Natur. J.	The Naturalists' Journal
Naturaleza	La Naturaleza. Periodico cientifico de la Sociedad Mexicana de Historia Natural
Naturalist (Yorks)	The Naturalist: Journal of the West Riding Consolidated Naturalists' Society
Naturaliste	Le Naturaliste
Nature	Nature
Naturf.	Der Naturforscher
Natur. Hist. Review	The Natural History Review and Quarterly Journal of Science
Naturhist. Notizen	Naturhistorische und chemisch-technische Notizen nach den neuesten Erfahrungen
Naturhist. Tidsskr.	Naturhistorisk Tidsskrift
Naturwiss. Umschau Chem. Ztg.	Naturwissenschaftliche Umschau der Chemiker-Zeitung
Natuurk Tijdschr.	Natuurkundige Tijdschrift, inhoudende Phijsica, Chemie, Pharmacie, Nat. Hist., &c., uitg. van wege het Genootschap: "Tot nut en vergenoegen," te Arnhem.
Nauche, J. Galvan.	Journal du Galvanisme, de Vaccine, etc.
Naval Archit. Trans.	Transactions of the Institution of Naval Architects
Naval Sci.	Naval Science: a Quarterly Magazine for promoting the improvement of Naval Architecture, Marine Engineering, Steam Navigation, and Seamanship
Neapel Zool. Sta., Fauna & Flora	Fauna und Flora des Golfes von Neapel und der angrenzenden Meeres-Abschnitte herausgegeben von der Zoologischen Station zu Neapel
Neapel Zool. Sta. Mitth.	Mittheilungen aus der Zoologischen Station zu Neapel
Nebraska Univ. Stud.	University Studies. Published by the University of Nebraska
Nederl. Archiv.	See Selenka
Nederl. Archief Natuurk.	Nederlandsch Archief voor Genees-en Natuurkunde
Nederl. Bot. Ver. Versl. en Meded.	See Nederl. Kruidk. Arch.
Nederl. Dierk. Ver. Tijdschr.	Tijdschrift der Nederlandsche Dierkundige Vereeniging
Nederl. Entom. Ver.	See Tijdschr. Ent.

Nederl. Kruidk. Archief.	Nederlandsch Kruidkundig Archief
Nederl. Lancet	Nederlandsch Lancet. Tijdschrift aan de praktische Chirurgie, etc.
Nederl. Tijdschr. Dierkunde	Nederlandsch Tijdschrift voor de Dierkunde, uitgegeven door het koninklijk Zoologisch Genootschap Natura Artis Magistra te Amsterdam
Nederl. Tijdschr. Geneesk.	Nederlandsch Tijdschrift voor Geneeskunde, tevens orgaan der Nederlandsche Maatschappij tot de Bevordering der Geneeskunst
Neuchatel Soc. Sci. Bull.	Bulletin de la Société des Sciences Naturelles de Neuchatel
Neues Bergmänn J.	Neues bergmännisches Journal
Neues Jahr. Min.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie
Neues Lausitz. Mag.	Neues Lausitizisches Magazin; unter Mitwirkung der Oberlausitzischen Gesellschaft der Wissenschaften
Neue med.-chir. Ztg.	Neue medicinisch-chirurgische Zeitung
Neues Nord. Archiv.	Neues nordisches Archif für Natur und Arzneikunde, verfasst von einer Gesellschaft nordischer Gelehrten
Neue Preuss. Provinz. Blätt.	Neue Preussische Privinzial-Blätter
Neu-Vorpommern Mitth.	Mittheilungen aus dem naturwissenschaftlichen Vereins für Neu-Vorpommern und Rügen in Greifswald
Newbury Field Club Trans.	Transactions of the Newbury District Field Club
Newcastle Chem. Soc. Trans.	Newcastle-upon-Tyne Chemical Society. Transactions
Newf. P.	Newfoundland Patent
Newman. Entom.	The Entomologist
Newport Natur. Hist. Soc. Proc.	Proceedings of the Newport Natural History Society
Nicholson J.	Journal of Natural Philosophy, Chemistry, and the Arts
Nick.	The Nickelodeon
Niederl. Archiv. Zool.	Niederländisches Archiv. für Zoologie
Niederösterr. Gewerb-Ver. Verh.	Verhandlungen des Niederösterreichischen Gewerbe-Vereins
Niederrhein. Ges. Naturk. Sitzber.	Sitzungsberichte der Niederrheinischen Gesellschaft für Natur- und Heilkunde zu Bonn
Niederrhein. Ges. Organ.	Organ für die gesammte Heilkunde; herausgegeben von der Niederrheinischen Gesellschaft für Natur- und Heilkunde zu Bonn
Nieuw Archief Wisk.	Nieuw Archief voor Wiskunde
Nimes Soc. Sci. Bull.	Bulletin de la Société d'Etude des Sciences Naturelles de Nimes
Nor. Amer. Med. Chir. Rev.	The North-American Medico-Chirurgical Review
Nor. Eng. Inst. Min. Engin. Trans.	North of England Institute of Mining and Mechanical Engineers. Transactions
Nor. Staff. Field Club Rep.	(The) North Staffordshire (Naturalists') Field Club (and Archaeological Society). Annual Report (and Transactions)
Nord. Braband, Handel. prov. Genoots.	Handelingen van het provinciaal Genootschap van Kunsten en Wetenschappen in Nord Braband
Nord France Soc. Linn. Bull.	Bulletin de la Société Linneenne du Nord de la France
Nord France Soc. Linn. Mem.	Memoires de la Société Linneenne du Nord de la France

Nord, Mem. Soc. Agric.	See Douai
Nord, Soc. Agric. Seance Publ.	Seance Publique de la Société d'Agriculture, Sciences, et Arts, etc., du departement du Nord
Nordamerik. Monatsber.	Nordamerikanischer Monatsbericht für Natur- und Heilkunde
Norddeut. Landwirth	Der norddeutsche Landwirth
Nordisches Archiv.	Nordisches (u. Neues Nordisches) Archiv. für Naturkunde und Arzneiwissenschaft
Norf. Norw. Natur. Soc. Trans.	Transactions of the Norfolk and Norwich Naturalists' Society
Normandie	See Caen
Normandie Soc. Linn. Bull.	Bulletin de la Société Linneenne de Normandie
Normandie Soc. Linn. Mem.	Memoires de la Société Linneenne de Normandie
Normandie Soc. Linn. Seance Publ.	Seance Publiques de la Société Linneenne de Normandie
Norsk Tidsk. Vid. Litt.	Norsk Tidskrift for Videnskab og Litteratur.
Norske Videnskab. Skrift.	Det Kongelige Norske Videnskabersselskabs Skrifter i det 19 de Aarhundrede
Northampton Natur. Hist. Soc. J.	Journal of the Northampton(shire) Natural History Society and Field Club
Northern J. Med.	Northern Journal of Medicine
Northumb. Natur. Hist. Soc. Trans.	Transactions of the Natural History Society of Northumberland, Durham, and Newcastle-upon-Tyne
Northwestern Drug.	Northwestern Druggist (The), Minneapolis
Norw. P.	Norwegian Patent
Notarisia	Notarisia. Commentarium Phycologicum. La Notarisia. Commentario Ficologico Generale. Parte speciale della Rivista Neptunia
Notices of Judgment, U. S. Dept. Agric.	Notices of Judgment, U. S. Department of Agriculture
Notiz. Archit. Ver. Niederrhein	Notizblatt des Architekten und Ingenieur Vereins für Niederrhein und Westfalen
Notiz. Riga	Notizblatt des technischen Vereins zu Riga
Nouv. Ann. Math.	Nouvelles Annales de Mathematiques
Nouv. Archiv. Miss. Sci.	Nouvelles Archives des Missions Scientifiques et Litteraires
Nouv. remedes	Nouveaux remedes, Paris
Nova Acta Acad. Nat. Curios.	Novorum Actorum Academiae Caesareae Leopoldino-Carolinae Germanicae Naturae Curiosorum
Nova Scotia Inst. Sci. Proc. & Trans.	(The) Proceedings and Transactions of the Nova Scotian Institute of (Natural) Science
Nova Scotia, Trans. Lit. Sci. Soc.	Transactions of the Literary and Scientific Society of Nova Scotia
Novitates Zool.	Novitates Zoologicae. A Journal of Zoology in connection with the Tring Museum
Nuov. Ann. Sci. Natur.	Nuovi Annali delle Scienze naturali
Nuov. Antol. Sci.	Nuova Antologia di Scienze, Lettere (Lettere, Scienze) ed Arti
Nuov. Cimento	Il Nuovo Cimento, Giornale di Fisica, di Chimica, e di Storia Naturale
Nuov. Giorn. Bot. Ital.	Nuovo Giornale Botanico Italiano (e Bullettino della Societa Botanica Italiana)
Nuov. Notarisia	La Nuova Notarisia. Rassegna (trimestrale) consacrata allo Studio delle Alghe (e Corollario alla "Sylloge Algarum Omnium")
Nürnb. Natur. Ges. Abh.	Abhandlungen der Naturhistorischen Gesellschaft zu Nürnberg
Nye Hygaea	Nye Hygaea

Nyt Mag. Naturvid.	Nyt Magazin for Naturvidenskaberne
Nyt Tidsskr. Fys. Kem.	Nyt Tidsskrift for Fysik og Kemi.
Oberhess. Ges. Ber.	Berichte der Oberhessischen Gesellschaft für Naturkunde und Heilkunde in Giessen
Odontol. Soc. Trans.	Transactions of the Odontological Society of Great Britain
Oesterr. Bot. Zts.	Oesterreichische Botanische Zeitschrift
Oesterr. Chem. Ztg.	Oesterreichische Chemiker Zeitung
Oesterr. landw. Wochenbl.	Oesterreichisches landwirtschaftliches Wochenblatt
Oesterr. Med. Jahr.	Medicinisches Jahrbuch des k. k. Oesterreichischen Staates
Oesterr. Med. Wochenschr.	Oesterreichische Medicinische Wochenschrift, als Ergänzungsblatt der medicinischen Jahrbücher
Oesterr. Wochenschr.	Oesterreichische Wochenschrift für Wissenschaft, Kunst, und öffentliches Leben
Oesterr. Zts. Berg. Hüttenw.	Oesterreichsche Zeitschrift für Berg- und Hüttenwesen
Oesterr.-ung. Zts. Zuckerind.	Oesterreichisch-ungarische Zeitschrift für Zuckerindustrie und Landwirtschaft
Off. Gaz.	Official Gazette, United States Patent Office
Offenbach. Ver. Naturk. Ber.	Bericht des Offenbacher Vereins für Naturkunde über seine Thätigkeit
Oil Colour J.	Oil and Colourman's Trade Journal
Oil, Paint Drug. Rep.	Oil, Paint and Drug Reporter
Oise	See Beauvais
Oise Mem. Soc. Acad.	Memoires de la Société Academique d'Archeologie, Sciences, et Arts du departement de l'Oise
Oken Isis	Isis, oder Encyclopädische Zeitung
Omaha Drug.	Omaha Druggist (The), Omaha
Omodei Ann. Univ.	Annali Universali di Medicina
Ontario Entom. Soc. Rep.	Report of the Entomological Society of Ontario
Oporto	See Porto
Ophthalm. Bibliothek	Ophthalmologische Bibliothek
Ophthalm. Hosp. Reports	Ophthalmic Hospital Reports and Journal of the Royal London Ophthalmic Hospital
Ophthalmic Rev.	The Ophthalmic Review: a Quarterly Journal of Ophthalmic Surgery and Science
Organ Rübenzuckerind.	Organ des Centralvereins für Rübenzuckerindustrie
Orgelb.	Die Orgelbauzeitung
Orleans Ann.	Annales de la Société Royale des Sciences, Belles-Lettres, et Arts d'Orleans
Orleans, Bull.	Bulletin des Sciences Physiques, Medicales, et d'Agriculture d'Orleans
Ornis	Ornis, oder das Neuste und Wichtigste der Vögelkunde, etc.
Ornith. Jahr.	Ornithologisches Jahrbuch
Ornith. Monatsber.	Ornithologische Monatsberichte
Ornithol.	The Ornithologist
Ornithol. Ool.	The Ornithologist and Oologist
Örsted Tidsskrift	Tidsskrift for Naturvidenskaberne
Orvos-Termesz. Ertes.	Orvos-Termeszettudomanyi Ertesitő a Kolozsvari Orvos-Termeszettudomanyi Tarsulat es az Erdelyi Museum-Egylet Termeszettudomanyi Szakosztalyanak az..szaküleseiröl..(Medical and Natural History Proceedings of the sections of the Klausenburg Medical and Natural History Society and of the Natural History section of the Museum Association of Transylvania

Osnabrück, Jahr.	Jahresbericht des Naturwissenschaftlichen Vereins zu Osnabrück
Ottawa Field-Natur. Club Trans.	Ottawa Field-Naturalists' Club Transactions
Ottawa Natur.	The Ottawa Naturalist
Ouest France Soc. Sci. Nat. Bull.	See Nantes...
Oversigt K. Danske Vidensk. Selsk. Forh.	Oversigt over det Kongelige Danske Videnskabernes Selskabs Forhandlinger
Pacific Drug. Rev.	Pacific Drug Review, Portland
Pacific Pharm.	Pacific Pharmacist
Padova, Mem. Acad.	Memorie dell' Accademia di Scienze, Lettere, ed Arti di Padova
Padova, Nuovi Saggi	Nuovi Saggi dell' Accademia di Scienze, Lettere, ed Arti di Padova
Padova, Rivista Period.	Rivista Periodica dei Lavori della I. R. Accademia di Scienze, Lettere, ed Arti di Padova
Padova, Soc. Sci. Atti	Atti della Societa Veneto-Trentina di Scienze naturali
Padova Soc. Sci. Bull.	Bullettino della Societa Veneto-Trentina di Scienze Naturali residente in Padova
Palermo Accad. Atti	Atti della Reale Accademia di Scienze, Lettere e Belle Arti di Palermo
Palermo Circ. Mat. Rend.	Rendiconti del Circolo Matematico di Palermo
Palermo, Effemeridi	Effermeridi scientifiche e letterarie per la Sicilia; coi Lavori del R. Instituto d'Incorraggiamento per la Sicilia
Palermo, Giorn. Sci. Natur.	Giornale di Scienze naturali ed economiche, pubblicato per Cura della Societa di Scienze naturali ed economiche di Palermo
Palermo, Mem. Spettrosc. Ital.	Memorie della Societa degli Spettroscopisti Italiani
Palermo Oss. Bull. Meteorol.	Bullettino Meteorologico del Reale Osservatorio di Palermo
Palermo Oss. Ossvz. Meteorol.	R. Osservatorio di Palermo. Stazioni di Valverde Osservazioni meteorologiche
Palomba, Raccolta	Raccolta di Lettere, etc., intonno alla Fisica ed alle Mathematiche
Palyamunkak	Palyamunkak. Termerzetlud (Prize Essays of the Hungarian Academy)
Pander, Beitr. Naturk.	Beiträge zur Naturkunde aus den Ostseeprovinzen Russlands
Paper	Paper
Paper-Maker Brit. Trade J.	Paper Maker and British Trade Journal
Paper Makers' Monthly J.	Paper Makers' Monthly Journal
Paper Making	Paper Making
Paper Mill	Paper Mill and Woodpulp News
Papers Naval Archit.	Papers on Naval Architecture and other subjects connected with naval science
Paper Trade J.	Paper Trade Journal
Papier-Fabr.	Papier-Fabrikant, Der
Papier Ztg.	Papier Zeitung
Papierhandel	Der Papierhandel
Papilio	Papilio
Papir J.	Papir Journalen
Par. P.	Paraguay Patent
Para, Mus. Hist. Natur. Bol.	Boletim do Museu Paraense de Historia Natural e Ethnographia
Paris, Acad. Med. Bull.	Bulletin de l'Academie de Medecine

Paris, Acad. Med. Mem.	Memoires de l'Academie de Medecine
Paris, Acad. Sci. Compt. rend.	Comptes Rendus hebdomadaires des Seances de l'Academie des Sciences
Paris, Acad. Sci. Mem.	Memoires de l'Academie des Sciences de l'Institut de France
Paris, Ann. Cerc. Med.	Annales du Cercle Medicale
Paris, Ann. Conserv.	Annales du Conservatoire des Arts et Metiers
Paris, Ann. Ecole Norm.	Annales scientifiques de l'Ecole Normale Superieure
Paris, Ann. Ponts Chauss.	Annales des Ponts et Chaussees. Memoires et documents relatifs a l'Art des Constructions et au Service de l'Ingenieur
Paris, Ann. Soc. Entom.	Annales de la Société Entomologique de France
Paris, Annaes Sci.	Annaes das Sciencias, etc., por huma Sociedade de Portuguezes residentes em Paris
Paris, Annu. Med. Chir. Hosp.	Annuaire medico chirurgical des Hopitaux, etc., de Paris
Paris, Annu. Soc. Met.	Annuaire de la Société Meteorologique de France
Paris, Anthropol. Soc. Bull.	Bulletin de la Société d'Anthropologie de Paris
Paris, Anthropol. Soc. Mem.	Memoires de la Société d'Anthropologie de Paris
Paris, Bull. Fac. Med.	Bulletins de la Faculte de Medecine de Paris et de la Société etablie dans son sein
Paris, Bull. Soc. Aerost.	Bulletin de la Société Aerostatique et Meteorologique de France
Paris, Bull. Soc. Sci. Natur.	Bulletin de la Société des Sciences Naturelles de France
Paris, Bur. Long. Annu.	Annuaire pour l'An...publie par le Bureau des Longitudes
Paris, Caus. Sci.	Causeries Scientifiques de la Société Zoologique de France
Paris, Club Alpin Franc. Annu.	Annuaire du Club Alpin Francais
Paris, Com. Intl. Carte Ciel Bull.	Institut de France. Academie des Sciences. Bulletin du Comite International Permanent pour l'Execution Photographique de la Carte du Ciel
Paris Congr. Bot. Act.	Actes du Congres International de Botanique tenu a Paris in aout 1867
Paris Congr. Bot. Compt. rend.	...Comptes Rendus...Congres International de Botanique et d'Horticulture
Paris, Congr. Med. Intl.	Congres Medical International de Paris, 1867
Paris, Ecole Norm. Ann.	Annales Scientifiques de l'Ecole Normale Superieure, publies sous les auspices du Ministre de l'Instruction Publique
Paris, Ecole Poly. Corresp.	Correspondance sur l'Ecole Polytechnique, a l'usage des Eleves de cette Ecole
Paris, Ecole Poly. J.	Journal de l'Ecole Polytechnique publie par le Conseil d'Instruction de cet Etablissement
Paris, Ethnog. Soc. Compt. rend.	Comptes Rendus des Seances de la Société d'Ethnographie Americaine et Orientale
Paris, Hautes Etudes Bibl.	Bibliotheque de l'Ecole des Hautes Etudes...Section des Sciences Naturelles
Paris, Ingen. Civ. Mem.	Memoires et Compte Rendu des Travaux de la Socéité des Ingenieurs Civils (de France)
Paris, J. Bot.	Journal de Botanique, par une Société de Botanistes
Paris, J. Chir.	Journal de Chirurgie
Paris, Lab. Histol. Trav.	Ecole Pratique des Hautes Etudes. Laboratoire d'Histologie du College de France. Travaux
Paris, Mem. Acad. Med.	Memoires de l'Academie (Royale) de Medecine
Paris, Mem. Acad. Sci.	Memoires de l'Academie des Sciences
Paris, Mem. Inst.	Memoires de la Classe des Sciences mathematiques et physiques de l'Institut

Paris, Mem. Soc. Savants	Memoires des Sociétés Savants et Litteraires de la Republique Francaise
Paris, Mem. Savants Etrang.	Memoires presentes par divers Savants a l'Academie des Sciences de l'Institut de France
Paris, Mem. Soc. Ethnol.	Memoires de la Société Ethnologique
Paris, Mem. Soc. Fac. Med.	Memoires de la Société de la Faculte de Medecine
Paris, Mem. Soc. Linn.	Memoires de la Société Linneenne de Paris
Paris, Mem. Soc. Med.	Memoires de la Société de Medecine
Paris, Mem. Soc. Med. Observ.	Memoires de la Société Medicale d'Observation
Paris, Mus. Hist. Natur. Ann.	Annales du Museum d'Histoire Naturelle
Paris, Mus. Hist. Natur. Archiv.	Archives du Museum d'Histoire Naturelle
Paris, Mus. Hist. Natur. Bull.	Bulletin du Museum d'Histoire Naturelle
Paris, Mus. Hist. Natur. Cent.	Centenaire de la Fondation du Museum d'Histoire Naturelle
Paris, Mus. Hist. Natur. Mem.	Memoires du Museum d'Histoire Naturelle
Paris, Mus. Hist. Natur. Nouv. Ann.	Nouvelles Annales du Museum d'Histoire Naturelle
Paris, Mus. Hist. Natur. Nouv. Archiv.	Nouvelles Archives du Museum d'Histoire Naturelle
Paris Obs. Ann.	Annales de l'Observatoire de Paris
Paris, Obs. Montsouris Annu.	(Ville de Paris.) Annuaire de l'Observatoire (municipal de Paris, dit Observatoire) de Montsouris...
Paris, Poids Mes. Proc.-Verb.	Comite International des Poids et Mesures. Proces-Verbaux des Seances
Paris, Poids Mes. Trav. Mem.	Travaux et Memoires du Bureau International des Poids et Mesures
Paris, Recueil Soc. Med. Observ.	Recueil des travaux de la Société Medicale d'Observation de Paris
Paris, Recueil. Trav. Soc. Med. Allemande	Recueil des Travaux lus a la Société Medicale Allemande de Paris
Paris, Soc. Acclim. Bull.	Bulletin de la Société Zoologique d'Acclimatation
Paris, Soc. Anat. Bull.	Bulletin de la Société Anatomique de Paris
Paris, Soc. Anthrop. Bull.	Bulletins de la Société d'Anthropologie de Paris
Paris, Soc. Anthrop. Mem.	Memoires de la Société d'Anthropologie de Paris
Paris, Soc. Biol. Mem.	Comptes Rendus des Seances et Memoires de la Société de Biologie
Paris, Soc. Chir. Bull.	Bulletin de la Société de Chirurgie de Paris
Paris, Soc. Chir. Mem.	Memoires de la Société de Chirurgie de Paris
Paris, Soc. Entom. Ann.	Annales de la Société Entomologique de France
Paris, Soc. Entom. Bull.	Bulletin de la Société Entomologique de France
Paris, Soc. Geogr. Bull.	Bulletin de la Société de Geographie
Paris, Soc. Geogr. Compt. rend.	Compte Rendu des Seances de la Société de Geographie et de la Commission Centrale
Paris, Soc. Hist. Natur. Mem.	Memoires de la Société d'Histoire Naturelle de Paris
Paris, Soc. Ing. Civ. Mem.	Memoires et Comptes Rendus des Travaux de la Société des Ingenieurs Civils
Paris Soc. Linn. Bull.	Bulletin mensuel de la Société Linneenne de Paris
Paris, Soc. Math. Bull.	Bulletin de la Société Mathematique de France
Paris, Soc. Med. Emul. Bull.	Bulletins de la Société Medicale d'Émulation
Paris, Soc. Med. Emul. Mem.	Memoires de la Société Medicale d'Émulation
Paris, Soc. Philom. Bull.	Bulletin des Sciences de la Société Philomathique de Paris

Paris, Soc. Philom. Mem. Cent.	Memoires publies par la Société Philomathique a l'occasion du Centenaire de sa Fondation, 1788–1888
Paris, Soc. Philom. Nouv. Bull.	Nouveau Bulletin des Sciences de la Société Philomatique de Paris
Paris, Soc. Philom. Proc. Verb.	Extraits des Proces-Verbaux des Seances de la Société Philomatique
Paris, Soc. Phys. Seances	Seances de la Société Francaise de Physique
Paris, Soc. Speleol. Mem.	Memoires de la Société de Speleologie
Paris Tow. Nauk Scisl. Pam.	Pamietnik Towarzystwa Nauk Scislych w Paryzu
Paris, Trav. Soc. Amat.	Notice des Travaux de la Société des Amatuers des Sciences physiques et naturelles de Paris
Parlatore, Giorn. Bot.	Giornale Botanico Italiano
Parma, Giorn. Soc. Med. Chir.	Giornale della Societa Medico-Chirurgica di Parma
Passau Ber. Nat. Ver.	...Bericht des Naturhistoischen Vereins in Passau für...
Passau, Jahr. Naturhist. Ver.	Jahresbericht des Naturhistorischen Vereins
Pathol. Soc. Trans.	Transactions of the Pathological Society of London
Pavia Ist. Bot. Atti	Atti dell' Istituto Botanico dell' Universita di Pavia. Seguito dell' Archivio Triennale del Laboratorio di Botanica Crittogamica
Pavia Lab. Crittog. Archiv.	Archivio del Laboratorio di Botanica Crittogamica presso la R. Universita di Pavia
Peabody Acad. Mem.	Memoirs of the Peabody Academy of Science
Peabody Acad. Report	Sixth Annual Report of the Trustees of the Peabody Academy of Science.
Penn. Univ. Publ.	Publications of the University of Pennsylvania
Penzance Soc. Trans.	Transactions of the Natural History and Antiquarian Society of Penzance
Perf. Essent. Oil Rec.	Perfumery and Essential Oil Record
Perthsh. Soc. Sci. Trans. & Proc.	Transactions and Proceedihgs of the Perthshire Society of Natural Science
Peru P.	Peruvian Patent
Pet. Nouv. Entom.	Petites Nouvelles Entomologiques
Petermann, Mitth.	Dr. A. Petermann's Mittheilungen aus Justus Perthes' Geographischer Anstalt
Peters, Zts.	Zeitschrift für populäre Mittheilungen aus dem Gebiete der Medicin, Chirurgie, und Pharmacie; in Verbindung mit einem Vereine von Aerzten und Pharmaceuten der Herzogthümer Schleswig und Holstein
Petroleum	Petroleum
Petroleum Gaz.	Petroleum Gazette
Petroleum Rev.	Petroleum Review
Pflüger, Archiv. Physiol.	Archiv. für die gesammte Physiologie des Menschen und der Thiere
Pharm.	Pharmakologie
Pharm.-Ber. Deut.-Arzbuch.	Pharmakopoe-Bericht. Die vegetablischen Drogen des Deutschen Arzneibuches, 5^{te}. Ausgabe, Caesar & Loretz, Halle
Pharm. Centr.	Pharmaceutisches Central-Blatt
Pharm. Centralh.	Pharmaceutische Centralhalle für Deutschland
Pharm. Era	Pharmaceutical Era
Pharm. J.	The Pharmaceutical Journal (and Transactions)
Pharm. Post	Pharmazeutische Post
Pharm. Weekblad	Pharmazeutische Weekblad
Pharm. Ztg.	Pharmazeutische Zeitung

Pharm. Zts.	Pharmazeutische Zeitschrift
Pharm. Zts. Russland	Pharmaceutische Zeitschrift für Russland
Phil. Mag.	Philosophical Magazine
Phil. Stud.	Philosophische Studien
Phil. Trans.	Philosophical Transactions of the Royal Society of London
Phila. Acad. Natur. Sci. J.	Journal of the Academy of Natural Sciences of Philadelphia
Phila., Acad. Natur. Sci. Proc.	Proceedings of the Academy of Natural Sciences of Philadelphia
Phila. Amer. Entom. Soc.	See Amer. Entom. Soc.
Phila. Coll. Pharm. Journ.	Journal of the Philadelphia College of Pharmacy
Phila. Eng. Club	Proceedings of the Engineers' Club of Philadelphia
Phila. Entom. News	Entomological News (and Proceedings of the Entomological Section of the Academy of Natural Sciences of Philadelphia)
Phila. Entom. Soc. Proc.	Proceedings of the Entomological Society of Philadelphia
Phila. Med. Mus.	Philadelphia Medical Museum
Phila. Med. Phys. J.	The Philadelphia Medical and Physical Journal
Phila. Phot.	The Philadelphia Photographer
Philippine J. Sci.	Philippine Journal of Science
Phot. Archiv	Photographisches Archiv
Phot. Bull.	Anthony's Photographic Bulletin
Phot. Chronik.	Photographische Chronik und allgemeine Photographen-Zeitung
Phot. J.	Wilhelm Horn's Photographische Journal
Phot. Corr. (Korr.)	Photographische Korrespondenz
Phot. Mag.	Photographisches Magazine
Phot. Mitth.	Photographische Mittheilungen
Phot. Monats.	Photographische Monatshefte
Phot. News	Photographic News
Phot. Rundsch.	Photographische Rundschau und Photographisches Centralblatt
Phot. Soc. J.	Journal of the Photographic Society of London
Phot. Soc. Trans.	Trans. of the Photographic Society of London
Phot. Times	The Photographic Times
Phot. Wochenbl.	Photographisches Wochenblatt
Phot. World	The Photographic World
Phot. Centr.	Photographisches Centralblatt
Phot. Ztg.	Deutsche Photographen-Zeitung
Phys. Rev.	Physical Review
Physikal.-Chem. Zentr.	Physikalisch-chemisches Zentralblatt
Physikal. Meddel.	Physikalske Meddelelser
Physikal. Zts.	Physikalische Zeitschrift
Physiol. Russe	Le Physiologiste Russe
Physiol. Soc. Proc.	See J. Physiol.
Phytologist	The Phytologist: a popular Botanical Miscellany
Pisa, Ann. Scuola Norm.	Annali della R. Scuola Normale Superiore di Pisa. Scienze Fisiche e Matematiche
Pisa, Ann. Univ. Tosc. Sci. Cosm.	Annali della Universita Toscana. Scienze Cosmologiche
Pisa, Miscell. Med. Chir.	Miscellanea medico-chirurgico-farmaceutiche raccolte in Pisa
Pisa, Nuov. Giorn.	Nuovo Giornale de' Letterati
Pisa Soc. Sci. Proc.	Atti della Société Toscana di Scienze Naturali residente in Pisa

Pisa Soc. Tosc. Atti (Mem.)	Atti della Societa Toscana di Scienze Naturali residente in Pisa. Memorie
Pisa Soc. Tosc. Atti (Proc. Verb.)	Arti della Societa Toscana di Scienze Naturali residente in Pisa. Processi Verbali
Pistoja, Atti Accad.	Atti della R. Accademia Pistojese di Scienze, Lettere, ed Arti; Memorie di Matematica e Fisca
Plant World	Plant World, The
Plata Mus. Anales	Anales del Museo de La Plata. Materiales para la Historia fisica y moral del Continente Sud-Americano
Plata Mus. Revista	Revista del Museo de La Plata
Plön Biol. Sta. Forschungsber.	Forschungsberichte aus der Biologischen Station zu Plön
Plymouth Inst. Trans.	Annual Reports and Transactions of the Plymouth Institution and Devon and Cornwall Natural History Society
Pogg. Ann.	Poggendorff's Annalen der Physik und Chemie
Pogg. Ann. Beibl.	Poggendorff's Annalen der Physik und Chemie Beiblätter
Poligrafo	Il Poligrafo: Giornale di Science, Lettere, ed Arti
Polit.	Il Politecnico
Pollichia, Jahr.	Jahresbericht der Pollichia, eines naturwissenschaftlichen Vereins der Baierischen Pfalz (der Rheinpfalz)
Polsk. Tow. Przyrod. Kopernika	See Kosmos (Lwow)
Poly. Centr.	Polytechnisches Centralblatt
Poly. Centralh.	Polytechnische Centralhalle
Poly. Mitth.	Polytechnische Mittheilungen
Poly. Notiz.	Polytechnisches Notizblatt
Polygraph. Centr.	Polygraphisches Centralblatt
Pommer, Zts.	Schweizerische Zeitschrift für Natur- und Heilkunde
Pop. Mag. Anthropol.	The Popular Magazine of Anthropology
Pop. Sci. Mon.	Popular Science Monthly
Popular Sci. Rev.	The Popular Science Review: a Quarterly Miscellany of entertaining and instructive articles on Scientific subjects
Pontif. Univ. Gregor.	Pontificia Universita Gregoriana. Continuazione del Bullettino Meteorologico dell' Observatorio del Cellegio Romano
Port. P.	Portuguese Patent
Portland, Soc. Natur. Hist. Proc.	Proceedings of the Portland Society of Natural History
Porto, Ann. Soc. Lit.	Annaes da Sociedade Lit. Portuense
Porto Soc. Instruc. Rev.	Revista da Sociedade de Instruccao do Porto
Potsdam Astrophys. Obs. Publ.	Publicationen des Astrophysikalischen Observatoriums zu Potsdam
Pottery Gaz.	Pottery Gazette
Pottery and Glass	Pottery and Glass
Power	Power
Prace Mat.-Fiz.	Prace Matematyczno-Fizyczne. (Mathematical and Physical Papers)
Pract. Drug.	Practical Druggist and Pharmaceutical Review of Reviews, New York
Pract. Mag.	The Practical Magazine (London)
Pract. Mechan. J.	The Practical Mechanics Journal
Practitioner	The Practitioner
Prag, Abh.	Pojednani Kral. Ceske Spolecnosti Nauk. Abhandlungen der Königl. Böhmischen Gesellschaft der Wissenschaften

Prag, Ceske Ak. Fr. Jos. Pam.	Pomatnik na oslavu padesaitketeho panovnickeho Jubilea jeho Velicenstva Cisare a Krale Frantiska Josefa I. Vydala Ceska Akademie Cisare Frantisks Josefa pro Vedy, Slovesnost a Umeni. (Memoira in celebration of the fifty years Jubilee of the reign of H. I. & R. M. Francis Joseph I. Published by the Bohemian Imperial Francis Joseph Academy of Science, Literature and Art)
Prag, Ceske Akad. Fr. Jos. Rozpr. (Trida 2)	Rozpravy Ceske Akademie Cisare Frantiska Josefa pro Vedy, Slovesnost a Umeni v Praze. (Trida II.) (Transactions of the Bohemian Imperial Francis Joseph Academy of Science, Literature and Art in Prague. Class II)
Prag. Fr. Jos. Acad. Sci. Bull.	Academie des Sciences de l'Empereur Francois Joseph I. Bulletin International
Prag, Jahr. Böhm. Mus.	Jahrbücher des Böhmischen Museums für Natur- und Länderkunde
Prag, Jahr. Realschule	Jahresbericht der k. k. Böhmischen Ober-Realschule zu Prag
Prag, Lotos Abh.	Abhandlungen des Deutschen Naturwissenschaftlich-Medicinischen Vereines für Böhmen "Lotos"
Prag, Monatschr. Mus.	Monatsschrift der Gessellschaft des vaterländischen Museums in Böhmen
Prag, Sitzber.	Zpravy o Zasedani (Vestnik) Kralovske Ceske Spolecnosti Nauk. Trida. Mathematicko-Prirodove-decka. Sitzungsberichte der Königl. Böhmischen Gesellschaft der Wissenschaften. Mathematisch-Naturwissenschaftliche Classe
Prag Sternw. Magn. Mereorol. Beob.	Magnetische und Meteorologische Beobachtungen an der K. K. Sternwarte zu Prag
Prag, Verh.	Verhandlungen der Gesellschaft des vaterländisches Museums in Böhmen
Prag, Vierteljahrschr.	Vierteljahrschrift für die praktische Heilkunde
Pressburg, Corresp. Blatt.	Correspondenzblatt des Vereins für Naturkunde zu Pressburg
Pressburg, Verh.	Verhandlungen des Vereins für Naturkunde zu Pressburg
Presse Sci.	Presse Scientifique des Deux Mondes
Preuss. Bot. Ver. Sitzber.	See Königsberg Schriften
Preuss. Geod. Inst. Publ.	Publication des Königl. Preuss. Geodätischen Instituts
Preuss. Geod. Inst. Veröff.	Veröffentlichung des Königl. Preussischen Geodatischen Instituts
Preuss. Landes-Oekon.-Kolleg. Archiv.	See Landw. Jbüch.
Pribram Bergakad	See Wien, Berg- u. Hüttenm. Jbuch.
Princeton Mus. Contr.	Contributions from the (E. M.) Museum of Geology and Archaeology of Princeton College
Pringsheim, Jahr. Wiss. Bot.	Jahrbücher für Wissenschaftliche Botanik
Print. Reg.	Printers' Register
Prog. agric. viti.	Progres agricole et viticole
Proc. Amer. Acad.	Proceedings of the American Academy of Arts Sciences
Proc. Amer. Inst. Elec. Eng.	Proceedings of the American Institute of Electrical Engineers
Proc. Amer. Micro. Soc.	Proceedings of the American Microscopical Society
Proc. Amer. Pharm. Assoc.	Proceedings of the American Pharmaceutical Association
Proc. Amer. Phil. Soc.	Proceedings of the American Philosophical Society

Proc. Amer. Soc. Civil Eng.	Proceedings of the American Society of Civil Engineers
Proc. Amer. Soc. Micro.	Proceedings of the American Society of Microscopists
Proc. Amer. Soc. Test. Mat.	Proceedings of the American Society for Testing Materials
Proc. Amer. Water Works Assoc.	Proceedings of American Water Works Association
Proc. Assoc. Off. Agric. Chem.	Proceedings of the Association of Official Agricultural Chemists, Washington
Proc. Austral. Inst. Min. Eng.	Proceedings Australian Institute of Mining Engineers
Proc. Cambr. Phil. Soc.	Proceedings of the Cambridge Philosophical Society
Proc. Chem. Soc.	Proceedings of the Chemical Society (London)
Proc. Eng. Soc. Western Penn.	Proceedings of the Engineers' Society of Western Pennsylvania
Proc. Inst. Civil Eng.	Proceedings of the Institution of Civil Engineers
Proc. Inst. Mech. Eng.	Proceedings of the Institution of Mechanical Engineers
Proc. Natl. Wholesale Drug. Assoc.	Proceedings of the National Wholesale Druggists' Association
Proc. Physiol. Soc.	Proceedings of the Physiological Society
Proc. Roy. Soc. Edinb.	Proceedings of the Royal Society of Edinburgh
Proc. Roy. Soc. London	Proceedings of the Royal Society of London
Proc. Roy. Soc. Med.	Proceedings of the Royal Society of Medicine
Proc. Soc. Exp. Biol. Med.	Proceedings of the Society for Experimental Biology and Medicine
Proc. U. S. Naval Inst.	Proceedings of U. S. Naval Institute
Progres Med.	Le Progres Medical. Journal de Medecine, de Chirurgie et de Pharmacie
Progressive Age	Progressive Age
Propogation ind.	La Propogation industrielle. Revue mensuelle illustre des inventions, machines, appareils et procedes de la France, etc.
Prov. Med. Assoc. J.	Journal of the Provincial Medical Association
Prov. Med. Surg. Assoc. Trans.	Transactions of the Provincial Medical and Surgical Association
Psyche	Psyche. Organ of the Cambridge Entomological Club
Psychol. Med. J.	Journal of Psychological Medicine
Publ. Carnegie Inst.	Publications of the Carnegie Institution of Washington
Publ. ind.	Publication industrielle des machines par Armengaud
Public Analysts Proc.	Proceedings of the Society of Public Analysts
Public Health	Public Health
Pulp Paper Mag. Can.	Pulp and Paper Magazine of Canada
Pure Products	Pure Products. Scientific Station for Pure Products, New York
Puy, Soc. Agric. Ann.	Annales de la Société d'Agriculture, Sciences, etc., du Puy
Quart. J. Chem. Soc.	Quarterly Journal of the Chemical Society
Quart. J. Dent. Sci.	Quarterly Journal of Dental Science.
Quart. J. exp. Physiol.	Quarterly Journal of experimental Physiology
Quart. J. Geol. Soc.	Quarterly Journal of the Geological Society
Quart. J. Math.	The Quarterly Journal of Pure and Applied Mathematics
Quart. J. Micro. Sci.	Quarterly Journal of Microscopical Science
Quart. J. Micro. Soc.	Quarterly Journal of the Microscopical Society
Quart. J. Sci.	The Journal of Science and the Arts Continued as the Quarterly Journal of Science, Literature, and Arts

Quebec, Lit. Hist. Soc. Trans.	Transactions of the Literary and Historical Society of Quebec
Queensl. P.	Queensland Patent
Queensl. Annu. Rep. Brit. N. Guinea	Annual Report on British New Guinea
Queensl. Natur. Hist. Soc. Trans.	Transactions of the Natural History Society of Queensland
Queensl. Mus. Ann.	Annals of the Queensland Museum
Queensl. Roy. Soc. Proc.	The Proceedings of the Royal Society of Queensland
Quekett Micro. Club J.	Journal of the Quekett Microscopical Club
Quetelet, Corresp. Math.	Correspondance Mathematique et Physique
Radium	Radium, Le
Railroad Eng. J.	The Railroad and Engineering Journal. The American Railroad Journal and Van Nostrand's Engineering Magazine have been consolidated in this publication
Ranuzzi, Annuario Geogr.	Annuario geographico Italiano
Rass. minerar.	Rassegna mineraria metallurgica e chimica
Rauch Staub	Rauch und Staub
Rayer, Archiv.	Archives de Medecine comparee
Reclam, Kosmos	Kosmos: Zeitschrift für angewandte Naturwissenschaften
Records Min.	Records of Mining
Recueil Math. (Moscou)	Recueil Mathematique. Publie par la Société Mathematique de Moscou
Rec. Trav. Chim. Pays-Bas	Recueil des Travaux Chimiques des Pays-Bas (et de la Belgique)
Rec. Zool. Suisse	Recueil Zoologique Suisse, comprenant l'Embryologie, l'Anatomie et l'Histologie comparees, la Physiologie, l'Ethologie, la Classification des Animaux vivants et fossiles
Regensburg Bot. Ges.	See Flora
Regensburg Bot. Ges. Denkschr.	Denkschriften der Königlich (Bayerischen) Botanischen Gesellschaft zu Regensburg
Regensburg, Bot. Ztg.	Botanische Zeitung; herausg. von der k. Baier. Botanischen Gesellschaft zu Regensburg
Regensburg, Korresp. Blatt.	Korrespondenz-Blatt des Zoologischmineralogischen Vereins in Regensburg
Reichert, Archiv.	Archiv für Anatomie, Physiologie, und wissenschaftliche Medicin
Reil, Archiv.	Archiv. für die Physiologie
Reimann's Ztg.	Reimann's Färberzeitung
Reims, Seances Acad.	Seances et Travaux de l'Academie de Reims
Rend. soc. chim. ital.	Rendiconti della societa chimica italiana
Rep.	Repertorium, Repertoire Repertory
Rep. Anal. Chem.	Repertorium der analytischen Chemie...Organ des Vereins Analytischer Chemiker
Rep. Anat. Physiol.	Repertoire generale d'Anatomie et de Physiologie pathologiques et de Clinique chirurgicale
Rep. Chim.	Repertoire generale de Chimie (1901–), G. Jaubert
Rep. Chim. pure (appl.)	Repertoire de Chimie pure (et appliquée) (Societe Chimique de Paris, 1859–1864)
Rep. Pat. Inv.	The Repertory of Patent Inventions and other discoveries and improvements in arts, manufactures and agriculture
Rep. Math.	Repertorium der literarischen Arbeiten aus dem Gebiéte der reinen und angewandten Mathematik

Rep. Meteorol.	Repertorium für Meteorologie, herausgegeben von der Kaiserlichen Akademie der Wissenschaften
Rep. Pharm.	Repertorium für die Pharmacie
Rep. Phys.	Repertorium der Physik
Rep. Phys.-Tech.	See Carl
Rep. Chem. Lab. Amer. Med. Ass.	Reports of the Chemical Laboratory of the American Medical Association, Chicago
Rep. Council Pharm. Chem.	Reports of the Council of Pharmacy and Chemistry, American Medical Association, Chicago
Rep. H. M. Insp. Expl.	Report of His Majesty's Inspectors of Explosives
Rep. N. Y. Bd. Pharm.	Report of the New York State Board of Pharmacy
Rev. Anthrop.	Revue d'Anthropologie
Rev. Artill.	Revue d'Artillerie
Rev. Biol. Nord France	Revue Biologique du Nord de la France
Rev. Bot.	Rev. de Botanique. Bulletin mensuel de la Société Francaise de Botanique
Rev. Bryol.	Revue Bryologique. Bulletin bimestriel consacre a l'Etude des Mousses et des Hepatiques
Rev. chim. ind.	Revue de chimie industrielle et La revue de physique et de chimie
Rev. Cours. Sci.	Revue des Cours Scientifiques de la France et de l'Etranger
Rev. deux Mondes	Revue des deux Mondes (Paris)
Rev. Entom.	Revue d'Entomologie publiee par la Société Francaise d'Entomologie
Rev. gen. Bot.	Revue generale de Botanique
Rev. gen. chim.	Revue generale de chimie pure et appliquee (G. Jaubert)
Rev. gen. lait	Revue generale du lait
Rev. gen. mat. color.	Revue generale de matieres colorantes et de leurs applications aux textiles
Rev. gen. sci.	Revue generale des sciences pure et appliquee
Rev. Hortic.	Revue Horticole, Journal d'Horticulture pratique
Rev. hyg. pol. sanitaire	Revue d'hygiene et de police sanitaire
Rev. Ind.	Revue Industrielle
Rev. Ind. Chim.	Revue des industries chimiques et agricoles
Rev. Mag. Zool.	Revue et Magazin de Zoologie, pure et appliquee
Rev. Maritime Colon.	Revue Maritime (et Coloniale)
Rev. Med. Chir.	Revue Medico-Chirurgicale de Paris
Rev. Med. Franc. Etrang.	Revue Medicale Francaise et Etrangere
Rev. Met.	Revue de Metallurgie
Rev. Mycol.	Revue Mycologique. Recueil trimestriel illustre consacre a l'Etude des Champignons
Rev. phot.	Revue de photographie
Rev. Quest. Sci.	Revue des Questions scientifiques publiee par la Société Scientifique de Bruxelles
Rev. Sci.	(la) Revue Scientifique (de la France et de l'Etranger. Revue des Cours Scientifiques)
Rev. Sci. Natur.	Revue des Sciences Naturelles
Rev. Soc. Hyg. Aliment.	Revue de la société scientifique d'Hygiene alimentaire et de l'alimentation rationelle de l'homme
Rev. Suisse Zool.	Revue Suisse de Zoologie (et) Annales (de la Société Zoologique Suisse et) du Musee d'Histoire Naturelle de Geneve
Rev. Univ. Mines	Revue universelle des Mines, de la Metallurgie, des Travaux Publics, des Sciences et des Arts Appliquee a l'Industrie. Annuaire de l'Association des Ingenieurs sortis de l'Ecole de Liege

Rev. Vit.	Revue Viticulture
Rev. Zool.	Revue Zoologique, par la Société Cuvierienne
Revista Brazil.	Revista Brazileira, Journal de Sciencias, Lettras, e Artes
Revista, Chim. pure app.	Revista de chimica pure applicada
Revista ind. agric. Tucuman	Revista industrial y agrocola de Tucuman
Revista Ligure	Revista Ligure, giornale di Lettere, Scienze, etc.
Revista Med. Chile	Revista medica de Chile
Revista Med. Cirug. Habana	Revista de Medicina y Cirugia, Habana
Revista Minera	Revista Minera, periodico cientifico e industrial
Revista real acad. cien. Madrid	Revista de la real academia de ciencias de Madrid
Revista Telegr.	Revista de Telegrafos
Revista Trim. Microgr.	Revista Trimestral Micrografica. Organo del Laboratorio Histologico de la Facultad de Medicina de Madrid
Rhea	Rhea, Zeitschrift für die gesammte Ornithologie
Rheinische Monatsschr.	Rheinische Monatsschrift für praktische Aerzte
Rheinl. Westphal.	See Bonn.
Rheinl. Westphal. Corresp.	Correspondenzblatt des Naturhistorischen Vereins der Preussischen Rheinlande und Westphalens
Rheinl. Westphal. Verh.	Verhandlungen des Naturhistorischen Vereins der Preussischen Rheinlande und Westphalens
Rheinl. Westphal. Sitzber.	Sitzungsbericht des Naturhistorischen Vereins der Preussischen Rheinlande und Westphalens
Rheinpfalz Pollichia Festschr.	Festschrift zur Fünfzigjährigen Stiftungsfeier der Pollichia, Naturwissenschaftlichen Vereines der Rheinpfalz
Rheinpfalz Pollichia Jahr.	Jahresbericht der Pollichia, eines Naturwissenschaftlichen Vereins der Rheinpfalz
Rheinpfalz Pollichia Mitth.	Mittheilungen der Pollichia, eines Naturwissenschaftlichen Vereins der Rheinpfalz
Rheinpfalz Pollichia Sep.-Ausg.	...Separat-Ausgabe der Pollichia, des Naturwissenschaftlichen Vereines der Pfalz
Rhodora	Rhodora. Journal of the New England Botanical Club
Riga, Arb. Naturf. Ver.	Arbeiten des Naturforschenden Vereins in Riga
Riga, Corresp. Blatt. Naturf. Ver.	Correspondenz-Blatt des Naturforschenden Vereins in Riga
Rio de Janeiro Archiv. Palestr.	Archivos da Palestra Scientifica do Rio de Janeiro
Rio de Janeiro Mus. Nac. Archiv.	Archivos do Museu Nacional do Rio de Janeiro
Rio de Janeiro Mus. Nac. Revista	Revista do Museu Nacional do Rio de Janeiro... (Seguimento aos Archivos do Museu Nacional)
Rio de Janeiro Obs. Annaes	(Annaes do Imperial Observatorio do Rio de Janeiro)
Rio de Janeiro Obs. Bol.	Boletim mensal do Observatorio do Rio de Janeiro
Rio de Janeiro Obs. Revista	Revista do Observatorio. Publicacao mensal do Imperial Observatorio do Rio de Janeiro
Rio, Revista	Revista tri mensal de Historia e Geographis: Journal do Instituto Historico e Geographico Brasileiro
Rio, Soc. Vell. Trabal.	Trabalhos da Sociedade Vellosiana (Bibliotheca Guanabarense)
Riv.	Rivista
Riv. Bolognese	Rivista Bolognese di Scienze e Lettere
Riv. Geogr. Ital.	Rivista Geografica Italiana (e Bolletino della Societa di Studi Geografici e Coloniali in Firenze)

Riv. Ital. Sci. Natur. Napoli	Rivista Italiana di Scienze Naturali e loro Applicazioni pubblicata per cura degli Aspiranti Naturalisti
Riv. Ital. Sci. Natur. Siena	Rivista Italiana di Scienze Naturali e Bollettino del Naturalista Collettore, Allevatore, Coltivatore
Riv. Mat.	Rivista di Matematica
Riv. Mineral. Crist.	Rivista di Mineralogia e Cristallografia Italiana
Riv. Patol. Veg.	Rivista di Patologia Vegetale
Riv. Sci.-Ind.	Rivista Scientifico-Industriale delle principali Scoperte ed Invenzioni fatte nelle Scienze e nelle Industrie
Riv. Sper. di Freniatria	Rivista Sperimentale di Freniatria e di Medicina legale...
Riv. Vit. Ital.	Rivista di Viticoltura ed Enologia Italiana...
Robin, J. Anat.	Journal de l'Anatomie et de la Physiologie normales et pathologiques de l'homme et des animaux
Rochelle	See under Charente-Inf.
Rochester Acad. Sci. Proc.	Proceedings of the Rochester New York Academy of Science
Rochester Trans. Elec. Med. Assoc.	Transactions of the National Electic Medical Association at its Third Meeting, at Rochester, U. S.
Rock Products	Rock Products
Röhr, Notizen	Notizen aus dem Gebiete der practischen Pharmacie
Rollett	See Graz.
Roma	See Congr. Med. Int. Atti, 1894
Roma, Atti Nuovi Lincei	Atti dell' Accademia Pontificia de' Nuovi Lincei
Roma, Atti Reale Accad.	Atti della Reale Accademia dei Lincei
Roma, Corrisp. Sci.	Corrispondenza Scientifica in Roma per le avanzamento delle Scienze, etc.
Roma Ist. Bot. Annuario	Annuario del R. Istituto Botanico di Roma
Roma Lab. Anat. Norm. Ric.	Ricerche fatte nel Laboratorio di Anatomia Normale della R. Universita di Roma
Roma, Nuovi Lincei Mem.	Memorie della Pontificia Accademia dei Nouvi Lincei
Roma, Oss. Coll. Rom. Mem.	Memorie del R. Osservatorio del Collegio Romano
Roma, R. Accad. Lincei	Atti della R. Accademia dei Lincei
(Roma), Soc. Ital. Mem.	Memorie di Mathematica e di Fisica della Societa Italiana delle Scienze
Roma, Soc. Studi Zool. Boll.	Bolletino della Societa Romana per gli Studi Zoologici
Roma, Specola Vaticana Pubbl.	Pubblicazioni della Specola Vaticana
Roma, Uff. Centr. Meterol. Ann.	Annali dell' Ufficio Centrale di Meterologia Italiana
Römer, Archiv Bot.	Archiv für die Botanik
Roser Wunderlich, Archiv	Archiv für physiologische Heilkunde. Continued as the Archiv. d. Heilk.
Rotterdam Nieuwe Verh.	Nieuwe Verhandelingen van het Bataafsch Genootschap der Proefondervindelijke Wijsbegeerte Rotterdam
Rouen, Bull. Soc. Emul.	Bulletins (des travaux) de la Société Libre d'Émulation de Rouen
Rouen, Soc. Sci. Bull.	Bulletin de la Société des Amis des Sciences Naturelles de Rouen
Rouen, Trav. Acad.	Precis analytique des Travaux de l' Academie des Sciences, Belles-Lettres, et Arts de Rouen
Roumanie Inst. Meteorol. Ann.	Annales de l'Institut Meteorologique de Roumanie Annalele Institutului Meteorologio al Romaniei
Roy. Engin. Papers	Papers on subjects connected with the duties of the Corps of Royal Engineers
Roy. Inst. J.	Journal of the Royal Institution of Great Britain

Roy. Inst. Proc.	Notices of the Proceedings at the Meetings of the Members of the Royal Institution of Great Britain, with Abstracts of the Discourses delivered at the Evening Meetings
Roy. School Naval Archit. Ann.	The annual of the Royal School of Naval Architecture and Marine Engineering
Roy. Soc. Proc.	Abstracts of the Papers printed in the Philosophical Transactions of the Royal Society of London, from 1800 to 1854 inclusive. Continued as the Proceedings of the Royal Society of London
Rugby, Natur. Hist. Soc. Reports	Reports of the Rugby School Natural History Society
Russ. Annu. Geol. Mineral.	Russian Annual of Geology and Mineralogy
Russ. Annuaire Mines	Annuaire du Journal des Mines de Russie
Russ. Chem. Soc: J.	Journal of the Russian Chemical Society
Russ. Geogr. Ges. Denkschr.	Denkschriften der Russischen Geographischen Gesell schaft zu St. Petersburg
Russ. J. exp. Landw.	Russiches Journal für experimentelle Landwirtschaft
Russ. Jahr. Pharm.	Russisches Jahrbuch der Pharmacie
Russ. P.	Russian Patent
Russ. Pharm. Zts.	Pharmaceutische Zeitschrift für Russland
Russ. Phys.-Chem. Soc. J.	Journal of the Russian Physico-Chemical Society of the Imperial University of St. Petersburg
Rust, Mag.	Magazin für die gesammte Heilkunde, etc.
S. Africa Chem. Metall. Soc.	The Journal of the Chemical and Metallurgical Society of South Africa
S. Africa Chem. Metall. Soc. Proc.	The Proceedings of the Chemical and Metallurgical Society of South Africa
S. Africa. Mus. Ann.	Annals of the South African Museum
S. Africa. Phil. Soc. Trans.	The Transactions of the South African Philosophical Society
S. Austral. P.	South Australian Patent
S. Austral. Roy. Soc. Mem.	Memoirs of the Royal Society of South Australia
S. Austral. Roy. Soc. Trans.	Tran sactions and Proceedings and Report of the Royal Society of South Australia
S. C. Med. Assoc. Trans.	Transactions of the South Carolina Medical Association
S. London Entom. Natur. Hist. Soc. Proc.	(Abstract of) Proceedings of the South London Entomological and Natural History Society
S. Wales Inst. Civ. Engin. Proc.	Proceedings of the South Wales Institute of Civil Engineers
S. Wales Roy. Inst. Report	The annual report of the Council of the Royal Institution of South Wales, with Appendix of Original Papers on Scientific Subjects
Sächs. Ingen. Ver. Mitth.	Mittheilungen des Sächsischen Ingenieur-Vereins; herausg. v. d. Verwaltungsrathe des Vereins
Sächs. Meteorol. Inst. Abh.	Abhandlungen des Königl. Sächs. Meteorologischen Institutes
Sachs. Thüring. Naturwiss. Ver.	See Zts. Naturwiss.
Salem	See Essex Institute
San Fernando Obs. Marina An.	Anales del Instituto y Observatorio de Marina de San Fernando
Sanitary Record	Sanitary Record and Journal of Municipal Engineering, The
Santiago Chile, Univ. Anales	(Republica de Chile.) Anales de la Universidad
Sao Paulo, Rev. Mus. Paulista	Revista do Museu Paulista

Saone-et-Loire Soc. Sci. Bull.	Bulletins de la Société des Sciences Naturelles de Saone-et-Loire
Saone-et-Loire Soc. Sci. Mem.	Memoires de la Société des Sciences Naturelle de Saone-et-Loire
Sarthe, Bull. Soc. Agric.	Bulletin de la Société d'Agriculture, Sciences, etc., de la Sarthe
Savoie Acad. Mem.	Memoires de l'Academie des Sciences, Belles-Lettres et Arts de Savoie
Savoie Soc. Hist. Natur. Bull.	Bulletins de la Société d'Histoire Naturelle de Savoie
Savoie Soc. Hist. Natur. (Compt. rend.)	Société d'Histoire Naturelle de Savoie a Chambery
Schaffhausen	See Schweizer. Entom. Gesell.
Scheik. Onderz.	See Utrecht. Scheik. Onderzoek
Schemnitz Bergakad.	See Wien, Berg- u. Hüttenm. Jahr.
Scherer, J. Chem.	Allgemeines Journal der Chemie
Schlesw.-Holst. Naturwiss. Ver. Schr.	Schriften des Naturwissenschaftlichen Vereins für Schleswig-Holstein
Schlömilch, Zts.	Zeitschrift für Mathematik und Physik
Schneider, Ann. Staatsarzneik.	Annalen der gessammten Staatsarzneikunde
School Mines Quart.	School of Mines, Quarterly, The
School of Mines, Records	Records of the School of Mines
Schrader, J. Bot.	Journal für die Botanik
Schröder, Berig. Zeevaart.	Berigten en Verhandelingen over eenige onderwerpen des Zeevaarts
Schröder, Verh. Zeevaart.	Verhandelingen en Berigten over eenige onderwerpen der Zeevaart-Kunde
Schuh Ind.	Schuh Industrie
Schumacher, Jahr.	Jahrbuch, (H. C. Schumacher, (1836–38))
Schwäb. Ges. Denkschr.	Denkschriften der Schwäbischen Gesellschaft der Aerzte und Naturforscher
Schwalbe	Ornithologische Section der k. k. Zoologisch-Botanischen Gesellschaft in Wien. Die Schwalbe. Berichte des Comites für Ornithologische Beobachtungs-Stationen in Oesterreich
Schweigger, J. (Schw. J.)	Journal für Chemie und Physik
Schweiz. Alpenclub Jahr.	Jahrbuch des Schweizer Alpenclub
Schweiz. Bot. Ges. Ber.	Berichte der Schweizerischen Botanischen Gesellschaft
Schweiz. Entom. Ges. Mitth.	Mittheilungen der Schweizerischen Entomologischen Gesellschaft
Schweiz. Ges. Neue Denkschr.	Neue Denkschriften der allgemeinen Schweizerischen Gesellschaft für die gesammten Naturwissenschaften
Schweiz. Ges. Verh.	Verhandlungen der Schweizerischen Gesellschaft für die geasmmten Naturwissenschaften
Schweiz. Monatsschr.	Schweizerische Monatsschrift für praktische Medizin
Schweiz. Naturf. Ges.	See Beitr. Kryptog. Schweiz.
Schweizer. Naturf. Ges. Verh.	Verhandlungen der Schweizerischen Naturforschenden Gesellschaft
Schweiz. Phot.-Ver.	See Wien, Phot. Correspond.
Schweiz. Poly. Zts.	Schweizerische polytechnische Zeitschrift. Unter Mitwirkung des Schweizerischen Polytechnikums, etc.
Schweiz. Wochenschr.	Schweizerisch Wochenschrift für Chemie und Pharmacie
Schweiz. Zts. Heilk.	Schweizerische Zeitschrift für Heilkunde
Sci.	Science
Sci. Abst.	Science Abstracts. Physics and Electrical Engineering
Sci. Amer.	Scientific American

Sci. Amer. Suppl.	Scientific American Supplement
Sci. Can.	Scientific Canadian
Sci. Ind. Bull. Roure-Bertrand Fils	Scientific et Industrial Bulletin Roure-Bertrand Fils
Sci. Proc. Roy. Dublin Soc.	Scientific Proceedings of the Royal Dublin Society
Sci. Rev.	The Scientific Review and Journal of the Inventors Institute
Sci. Trans. Roy. Dublin Soc.	Scientific Transactions of the Royal Dublin Society
Scienz. Ital. Congr.	Nuovo Congresso degli Scienziati Italiani in Venezia; porzione geologica
Sclater, Ibis	The Ibis, a Magazine of General Ornithology
Scott. Arbor. Soc. Trans.	Transactions of the Scottish Arboricultural Society
Scott. Geogr. Mag.	The Scottish Geographical Magazine
Scott. Meteorol. Soc. J.	Journal of the Scottish Meteorological Society
Scott. Micro. Soc. Proc. & Trans.	Proceedings and Transactions of the Scottish Microscopical Society
Scott. Natur.	A Magazine of Scottish Natural History (and Journal of the Perthshire Society of Natural Science)
Scott. Soc. Arts Trans.	Transactions of the Royal Scottish Society of Arts
Seeman, J. Bot.	The Journal of Botany, British and Foreign
Seifenfabr.	Seifenfabrikant, Der
Seifens. Ztg.	Seifensieder Zeitung und Revue über die Harz, Fett und Oelindustrie
Seine (Dep. de la)	See (France) Soc. Agr. Mem.
Seine, Mem. Soc. Agric.	Memoires d'Agriculture par la Société Agricole de la Seine
Seine-et-Oise, Mem.	Memoires de la Société des Sciences Naturelles de Seine et Oise
Seism. J. Japan	Seismological Journal of Japan
Selenka, Archiv Zool.	Nederländisches Archiv für Zoologie
Semi-Ann. Rep. Schimmel & Co.	Semi-Annual Report, Schimmel & Co., Miltitz
Senckenberg. Naturf. Ges. Abh.	Abhandlungen herausg. von der Senckenbergischen Naturforschenden Gesellschaft
Senckenberg, Naturf. Ges. Ber.	Bericht über die Senckenbergische naturforschende Gesellschaft in Frankfurt am Main
Shanghai, J.	Journal of the North-China Branch of the Royal Asiatic Society
Shanghai, J. Lit. Soc.	Journal of the Literary and Scientific Society of Shanghai
Shoe Lea. Reporter	Shoe and Leather Reporter
Shropsh. Soc. Trans.	Transactions of the Shropshire Archaeological and Natural History Society
Sicilia, Atti Soc. Acclim.	Atti della Societa di Acclimazione e di Agricoltura in Sicilia
Sidereal Messenger	The Sidereal Messenger
Siebenb. Karpath. - Ver. Jahr.	Jahrbuch des Siebenbürgischen Karpathen-Vereins
Siebold, J. Geburtshülfe	Journal für die Geburtshülfe, Frauenzimmer, etc., von Elias von Siebold
Siebold Kölliker, Zts.	Zeitschrift für wissenschaftliche Zoologie
Siebold, Lucina	Lucina; eine Zeitschrift zur Vervollkommung der Entbindungskunst
Siena, Atti Accad.	Atti dell' Accademia delle Scienze di Siena detta de' Fisio-critici
Silbermann, Rev. Entom.	Revue Entomologique

Silliman, J.	The American Journal of Science and Arts
Singapore Roy. Asiat. Soc. J.	Journal of the Straits Branch of the Royal Asiatic Society. Singapore
Sitzber. kais. Akad. Wiss. Wien.	Sitzungsberichte der kaiserlichen Akademie der Wissenschaften, Wien (Mathematisch-naturwissenschaftliche Klass) Abteilungen I, IIa, IIb, III
Sitzb. könig Akad. München	Sitzungsberichte der königlich bayerischen Akademie der Wissenschaften zu München
Sitzber. königl. Akad. Wiss. Berlin	Sitzungsber der königlich preussischen Akademie der Wissenschaften zu Berlin
Sitzber. königl. preuss. Akad.	Sitzungsberichte der königlich preussischen Akademie der Wissenschaften
Skand. Archiv Physiol.	Skandinavisches Archiv für Physiologie
Skand. Naturf. Förh.	Förhandlingar vid det af Skandinaviska Naturforskare och Läkare hallna Möte i Götheborg
Skand. Naturf. Mod. Forh.	Forhandlingerne ved de Skandinaviske Naturforskeres 11te Mode i Kjobenhavn fra den 3die til den 9de Juli, 1873
Skand. Natur. Möt. Förh.	Förhandlingar vid de Skandinaviska Naturforskarnes Tolfte Möte i Stockholm fran den 7 till den 14 Juli, 1880
Skandia	Skandia. Tidskrift för Vetenskap och Konst; utgifven af Svenska Litteratur-Föreningen
Skofitz	See Oesterreich. Botan. Zeitschr.
Skofitz, Bot. Wochenbl.	Oesterreichisches Botanisches Wochenblatt
Skofits, Bot. Zts.	Oesterreichische Botanische Zeitschrift
Smithsonian Contrib.	Smithsonian Contributions to Knowledge
Smithsonian Inst. Astrophys. Obs. Ann.	Annals of the Astrophysical Observatory of the Smithsonian Institution
Smithsonian Inst. Bur. Ethnol. Report	Annual Report of the Bureau of (American) Ethnology to the Secretary of the Smithsonian Institution
Smithsonian Misc. Coll.	Smithsonian Miscellaneous Collections
Smithsonian Report	Annual Report of the Board of Regents of the Smithsonian Institution, showing the Operations, Expenditures and Condition of the Institution
Snelling's Phot. J.	Snelling's Photographisches Journal
Soc. Bot. Ital Bull.	See Nuovo Giorn. Bot. Ital.
Soc. Broteriana	See Coimbra, Soc. Broter. Biol.
Soc. Elvet. Sci., Naturf. Atti	See Schweiz. Naturf. Ges. Verh.
Soc. Entom. Ross. Horae	Horae Societatis Entomologicae Rossicae variis sermonibus in Rossia usitatis editae
Soc. Franc. Bot.	See Rev. Bot.
Soc. Franc. Entom.	See Rev. Ent.
Soc. Freniatr. Ital.	See Riv. Sper. di Freniatria
Soc. Geogr. Finland	See Fennia
Soc. Helvet. Actes.	Actes de la Société Helvetique des Sciences Naturelles
Soc. Helvet. Sci. Naturf. Act.	See Schweiz. Natf. Ges. Verh.
Soc. Ital. Antrop.	See Arch. Antropologia
Soc. Ital. Fis.	See Nuovo Cimento
Soc. Ital. Micro. Boll.	See Acireale, Soc. Ital. Micr. Boll.
Soc. Ital. Sci.	See (Roma), Soc. Ital. Mem.
Soc. Ital. Sci. Nat.	See Milano, Soc. Ital.
Soc. Ligust. Sci. Natur. Geogr.	See Genova, Soc. Ligust. Atti
Soc. Malacol. France	See Ann. Malacol.

Soc. Malacol. Ital. Bull.	See Bull. Malacol. Ital.
Soc. Meteorol. Ital.	See Moncalieri Oss. Boll.
Soc. Mex. Hist. Natur.	See Naturaleza
Soc. Napoli	Societa reale di Napoli. Rendiconto dell' Academia delle Scienze fisiche e mathematiche
Soc. Nat. Sicil.	See Nat. Sicil.
Soc. Pharm. Anvers	See J. de Pharm.
Soc. Public Analysts	See Analyst
Soc. Speleol.	See Spelunca, Paris
Soc. Telegr.-Engin. Elect.	See Telegr. Eng. J.
Soc. Tosc. Sci. Nat.	See Pisa Soc. Tosc.
Soc. Ven.-Trent. Sci. Nat.	See Padova Soc. Sci.
Soc. Zool. Suisse Ann.	See Rev. Suisse: Zool.
Soc. Zool. Tokyo	See Annot. Zool. Jap.
Somerset. Archaeol. Soc. Proc.	Proceedings of the Somersetshire Archaeological and Natural History Society
Somerset. Sov. Proc.	Somersetshire Archaeological and Natural History Society's Proceedings
Somme (Dep. de la)	See under Amiens
Southern Pharm. J.	Southern Pharmaceutical Journal
Span. P.	Spanish Patent
Spatula	Saptula (The), Boston
Spelunca. Paris	Spelunca. Bulletin de la Société de Speleologie
Sperimentale	Lo Sperimentale. Giornale Italiano di Scienze Meidche
Spettatore Vesuvio	Lo Spettatore del Vesuvio e de' Campi Flegrei
Spettrosc. Ital. Mem.	Memorie della Societa degli Spettroscopisti Italiani
Spongia, Comm. Med.	Commentarii di Medicina
Sprechsaal	Sprechsaal
Spregnel, Jahr.	Jahrbücher der Gewächskunde
Sprengst. Waffen Mun.	Sprengstoffe, Waffen und Munition
St. Andrew's Med. Grad. Assoc. Trans.	Transactions of the St. Andrew's Medical Graduates Association
St. Barthol. Hosp. Reports	St. Bartholomew's Hospital Reports
St. Etienne, Bull. Soc. Ind. Mineral	Bulletin de la Société de l'Industrie Minerale
St. Gallen, Ber. Naturwiss. Ges.	Berichte über die Thätigkeit der St. Gallischen Naturwissenschaftlichen Gesellschaft
St. Louis, Bot. Gard. Report	Missouri Botanical Garden Report
St. Louis, Trans. Acad. Sci.	The Transactions of the Academy of Science of St. Louis
St. Petersb. Acad. Sci. Bull.	Bulletin scientifique publie par l'Academie Imperiale des Sciences de St. Petersbourg
St. Petersb. Acad. Sci. Compt. rend.	Compte Rendu de l'Academie Imperiale des Sciences de St. Petersbourg
St. Petersb. Acad. Sci. Mem.	Memoires de l'Academie Imperiale des Sciences de St. Petersbourg
St. Petersb. Acad. Sci. Nova Acta.	Nova Acta Academiae Scientiarum Imperialis Petropolitanae
St. Petersb. Acad. Sci. Recueil	Recueil des Actes des Seances Publiques de l'Academie Imperiale des Sciences de St. Petersbourg
St. Petersb. Ann. Mines Russ.	Annuaire du Journal des Mines de Russie
St. Petersb. Archiv. Sci. Biol.	Archives des Sciences Biologiques publiees par l'Institut Imperial de Medecine Experimentale a St. Petersbourg
St. Petersb., Congr. Bot. Bull.	Bulletin du Congres International de Botanique et d'Horticulture de St. Petersbourg le 6/18, le 8/20 et le 10/22 Mai 1869

St. Petersb. Inst. Med. Exper.	See St. Petersb. Arch. Sci. Biol.
St. Petersb. Med. Zts.	St. Petersburger Medicinische Zeitschrift
St. Petersb. Med. Wochenschr.	St. Petersburger Medicinische Wochenschrift
St. Petersb. Mem. Savants Etrang.	Memoires presentes a l' Academie Imperiale des Sciences de St. Petersbourg par divers Savants
St. Petersb. Mineral. Ges. Verh.	Verhandlungen der Russisch-Kaiserlichen Mineralogischen Gesellschaft zu St. Petersbourg
St. Petersb., Russe Geogr. Mem. (Geogr.)	Memoirs de la Société Imperiale Russe de Geographie Section de Geographie generale
St. Petersb., Russ. Geogr. Soc. Bull.	Bulletins of the Imperial Russian Geographical Society
St. Petersb. Schr. Mineral.	Schriften der in St. Petersburg gestifteten Kaiserlich-Russischen Gesellschaft für die gesammte Mineralogie
St. Petersb. Verh. Mineral. Ges.	Verhandlungen der Kaiserlich-Russischen Mineralogischen Gesellschaft zu St. Petersburg
St. Petersb. Verm. Abh.	Vermischte Abhandlungen aus dem Gebiete der Heilkunde von einer Gesellschaft pract. Aerzte zu St. Petersburg. Additional title in 1835, Medizinisch-praktische Abhandlung von Deutschen in Russland lebenden Aerzten. Continued as the Neue Abhandlung St. Petersburg
St. Quentin, Ann.	Annales Agricoles du department de l'Aisne, publiees par la Société des Sciences, Arts, Belles-Lettres, et Agriculture de St. Quentin. Annales Scientifiques, Agricoles, et Industrielles du departement de l'Aisne (Société Academique de Saint Quentin)
St. Quentin, Mem.	Memoires de la Société des Sciences, Arts, Belles-Lettres, et Agriculture de la ville de St. Quentin
St. Quentin, Seances Publ.	Société des Sciences, Arts, Belles-Lettres, et Agriculture de la ville de St. Quentin: Seances publiques.
St. Quentin, Travaux	Société Academique des Sciences, Arts, Belles-Lettres, et Agriculture de St. Quentin (Aisne)
St. Thomas's Hosp. Reports	St. Thomas's Hospital Reports
Stahl Eisen (Zts.)	Stahl und Eisen, Zeitschrift für das deutsche Eisenhüttenwesen
Stavanger Mus. Aarsber.	Stavanger Museums Aarsberetning
Staz. sper. agrar. ital.	Stazioni sperimentali agraria italiana, La
Steiermark. Geog. Mont. Ver. Ber.	Bericht des Geognostisch-montanistischen Vereins für Steiermark
Steiermark Mitth.	Mittheilungen des Naturwissenschaftlichen Vereines für Steiermark
Steiermark. Mont. Lehranst. Jahr.	Die Steiermarkisch ständische montanistische Lehranstalt zu Vordernberg
Stein, Ann.	Annalen der Geburtshülfe überhaupt und der Entbindungsanstalt zu Marburg insbesondere
Stettin, Entom. Ztg.	Entomologische Zeitung; herausg. v. d. Entomologischen Vereine zu Stettin
Steyermärk. Zts.	Steyermärkische Zeitschrift
Stirling Field Club Trans.	Stirling Field Club.... Transactions
Stirling Soc. Trans.	Stirling Natural History and Archaeological Society. Transactions
Stockholm, Akad. Handl.	Kongliga Svenska Vetenskaps Akademiens Handlingar
Stockholm, Bihang Akad. Handl.	Bihang till Kongl. Svenska Vetenskaps Akademiens Handlingar
Stockholm Bot. Sällsk.	See Bot. Centrbl.

Stockholm Entom. För.	See Ent. Tidskr.
Stockholm, Horti Bergiani Acta	Acta Horti Bergiani. Meddelanden fran Kongl. Svenska Vetenskaps-Akademiens Trädgard Bergielund utgifna af Bergianska Stiftelser
Stockholm, Öfversigt	Öfversigt af Kongl. Vetenskaps Akademiens Förhandlingar
Stockholm Physiol. Lab. Mitth.	Mittheilungen vom Physiologischen Laboratorium des Carolinischen Medico-Chirurgischen Instituts in Stockholm
Stockholm, Svenska Läk. Sällsk Handl.	Handlingar ved Svenska Läkare-Sällskapet
Stockholm, Vet. Akad. Lefnadsteckn.	Lefnadsteckningar öfver Kongl. Svenska Vetenskaps-Akademiens efter ar 1854 aflidna Ledamöter
Stockholm, Ymer	Ymer. Tidskrift utgifven af Svenska Sällskapet för Antropologi och Geografi
Strasbourg Soc. Hist. Natur. Mem.	Memoires de la Société du Museum d'Histoire Naturelle de Strasbourg
Strasbourg Soc. Sci. Bull.	Bulletin de la Société des Sciences Naturelles de Strasbourg
Strasbourg Soc. Sci. J.	Journal de la Société des Sciences, Agriculture, et Arts, du departement du Bas-Rhin
Strasbourg Soc. Sci. Mem.	Memoires de la Société des Sciences, Agriculture, et Arts, de Strasbourg
Stray Feathers	Stray feathers.. A journal of Ornithology for India and its dependencies
Stricker	See Medizin. Jahr.
Sts. Settl. P.	Straits Settlement Patent
Student	The Student and Intellectual Observer of Science, Literature, and Art
Sturgeon, Ann. Elect.	Annals of Electricity, Magnetism, and Chemistry, and Guardian of Experimental Science
Sturgeon, Ann. Phil.	Annals of Philosophical Discovery and Monthly Reporter of the Progress of Practical Science
Sucr.	La sucrerie indigene
Sucr. Belge	Sucrerie Belge, La
Sucr. ind. colon.	Sucrerie indigene et colonaile, La
Suddeut. Apoth. Ztg.	Suddeutsche Apotheker Zeitung
Suisse Soc. Zool. Ann.	See Rev. Suisse Zool.
Surveyor	Surveyor and Municipal and County Engineer, The
Sussex Natur. Hist. Soc. Proc.	See Brighton Nat. Hist. Soc. Proc.
Svea	Svea. Tijdskrift för Vetenskap och Konst
Svensk farm. Tidskr.	Svensk farmaceutisk Tidskrift, Stockholm
Svensk Kem. Tidskr.	Svensk Kemisk Tidskrift
Svenska Läk. Sällsk. Forh.	Forhandlingar ved Svenska Läkare-Sällskapets Sammankomster
Svenska Mosskulturför.	Svenska Mosskulturföreningens .
Svenska Sällsk. Antrop. & Geogr.	See Stockh., Ymer
Swart, Verh.	Verhandelingen en Berigten betrekkelijk het Zeewezen en de Zeewaartkunde
Swed. P.	Swedish Patent
Swiss P.	Swiss Patent
Sydney	See New South Wales
Sydney Aust. Mus. Mem.	The Australian Museum, Sydney. Memoirs
Sydney, Austral. Mus Records	Records of the Australian Museum
Symons, Meteorol. Mag.	Symon's monthly Meteorological Magazine
Tablettes Zool.	Tablettes Zoologiques

Tagbl. Frankf. Naturf.	Tageblatt Frankfurter Naturforscher
Taprobanian	The Taprobanian, a Dravidian Journal of Oriental Studies in and around Ceylon, in Natural History, Archaeology, Philology, History
Tasmania J. Natur. Sci.	The Tasmanian Journal of Natural Science, Agriculture, Statistics, etc.
Tasmania P.	Tasmanian Patent
Tasmania, Roy. Soc. Monthly Not.	Monthly Notices of Papers and Proceedings of the Royal Society of Tasmania
Tasmania, Roy. Soc. Reports	Reports of the Royal Society of Tasmania
Taylor, Sci. Mem.	Scientific Memoirs, selected from the Transactions of Foreign Academies and Learned Societies and from Foreign Journals
Tech. Blätter	Technische Blätter. Vierteljahrschrift des Deutschen Polytechnischen Vereins in Böhmen
Tech. Chem. Jahr.	Technisch-Chemisches Jahrbuch (Biedermann)
Tech. Gemeindebl.	Technisches Gemeindeblatt
Technikum	Technikum des Ledermarkts
Technol.	Le Technologiste (F. Malepeyre)
Technol. Quart.	Technology Quarterly
Teign Field Club Proc.	Reports of the Proceedings of the Teign Naturalists' Field Club
Tekn. Tidskr.	Teknisk Tidskrift
Telegr. Eng. J.	Journal of the Society of Telegraph-Engineers and Electricians
Telegr. J.	The Telegraphic Journal and Electrical Review
Telegr. Ver. Zts.	Zeitschrift des Deutsch-österreichischen Telegraphen-Vereins
Temminck, Verh.	Verhandelingen over de natuurlijke Geschiedenis der Nederlandsche overzeesche bezittingen, door de leden der Natuurkundige Commissie in Oost-Indie en andere schrijvers
Termr. Füz.	Termeszetrajzi Füzetek...Kiadja a Magyar Nemzeti Muzeum. (Natural History Magazine...published by the Hungarian National Museum)
Termt. Közlön.	Termeszettudomanyi Közlöny...Kiadja a K. M. Termeszettudomanyi Tarsulat. (Natural Science Papers...Published by the Royal Hungarian Natural Science Society)
Terrestrial Magn.	Terrestrial Magnetism (and Atmospheric Electricity). An International Quarterly Journal
Texas Acad. Sci. Trans.	Transactions of the Texas Academy of Science
Text. Amer.	Textile American
Text. Col.	The Textile Colorist
Text. Färb. Ztg.	Textil und Färberei-Zeitung
Text. Mfr.	The Textile Manufacturer
Text. Rec.	The Textile Record
Text. World Rec.	Textile World Record
Text. Ztg.	Textil Zeitung
Textilfreund	Der Textilfreund
Teyler's Verh.	Geologische Verhandel af Antwoord af de in 1828 uitgeschrevene en in 1830 herhaalde Prysvraag: Wat men van Geologie, etc.
Therap. Gaz.	The Therapeutic Gazette
Therap. Monats.	Therapeutische Monatshefte
Therap. Neuheit	Therapeutischen Neuheiten, Leipzig
Therapist	Therapist (The) London

Thomson, Ann. Phil.	Annals of Philosophy, or Magazine of Chemistry, Mineralogy, Mechanics, and the Arts
Thomson, Archiv. Entom.	Archives Entomologiques
Thomson, Rec.	Records of General Science
Thonind. Ztg.	Thonindustrie-Zeitung
Throndhjem, Skrifter	Der Kongelige Norske Videnskabers-Selskabs Skrifter i det 19 de Aarhundrede
Tidskr. Kemi. Farm. Terapi	Tidskrfit for Kemi Farmaci Terapi
Tidskr. Mat.	Tidsskrift for Matematik
Tidskr. Mat. Fys.	Tidskrift för Matematik och Fysik, tillegnad den Svenska Elementar-Undervisningen
Tidskr. Phys. Chem.	Tidskrift for Physik og Chemi samt disse Videnskabers Anvendelse
Tiedemann, Zts.	Zeitschrift für Physiologie
Tijdschr. Entom.	Tijdschrift voor Entomologie; uitgegeven door de Nederlandsche Entomologische Vereeniging
Tijschr. Genootsch. Vis. Unita	Tijdschrift voor Genees-, Heel-, Verlos-, en Scheikundige Wetenschappen, van Wege et Genootschap: "Vis Unita Fortior," te Hoorn.
Tijdschr. Ing.	Tijdschrift van het Koninklijk Instituut van Ingenieurs
Tijdschr. nijv.	Tijdschrift ter befordering van nijverhed
Tijdstroom.	De Tijdstroom; Maandschrift gewijd van Wetenschap, etc.
Tilesius, Jahr.	Jahrbuch der Naturgeschichte zur Anzeige und Prüfung
Timehri	Timehri being the Journal of the Royal Agricultural and Commercial Society of British Guiana
Tirol, Ber. Ver. Durchf.	Bericht über die General-Versammlung des Vereins zur geogr. montan. Durchforschung des Landes Tirol, etc.
Tischl. Ztg.	Deutsche Tischlerzeitung
Tokio Univ. Mem.	Memoirs of the Science Department, University of Tokio, Japan
Tokyo Bot. Soc.	See Bot. Mag., Tokyo
Tokyo, Coll. Sci. J.	The Journal of the College of Science, Imperial University, Japan
Tokyo Geogr. Soc. J.	Journal of the Tokio Geographical Society
Tonind. Ztg.	Tonindustrie Zeitung
Töpfer Ztg.	Deutsche Töpfer und Ziegler Zeitung
Torino, Accad. Sci. Atti	Atti della R. Accademia delle Scienze di Torino
Torino, Accad. Sci. Mem.	Memoire della R. Accademia delle Scienze di Torino
Torino, Ann. Clin.	Annali Clinici
Torino, Lavori Sci. Fis. Mat.	Notizia storica dei lavori fatti dalla Classe di Scienze Fisiche e Mathematiche della R. Accademia delle Scienze negli anni 1864–65
Torino Mus. Boll.	Bollettino dei Musei di Zoologia ed Anatomia comparata della R. Universita di Torino
Torrey Bot. Club Bull.	Bulletin of the Torrey Botanical Club
Torrey Bot. Club Mem.	Memoirs of the Torrey Botanical Club
Tortolini, Ann.	Annali di Scienze, Matematiche, e Fisiche
Toulouse Acad. Sci. Bull.	Bulletin de l'Academie des Sciences, Inscriptions et Belles-Lettres de Toulouse
Toulouse, Acad. Sci. Mem.	Memoires de l'Academie des Sciences, Inscriptions et Belles-Lettres de Toulouse
Toulouse Fac. Sci. Ann.	Annales de la Faculte des Sciences de Toulouse, pour les Sciences Mathematiques et les Sciences Physiques
Toulouse Obs. Ann.	Annales de l'Observatoire Astronomique, Magnetique et Meteorologique de Toulouse.

Toulouse Soc. Hist. Natur. Bull.	Bulletin de la Société d'Histoire Naturelle de Toulouse
Toulouse Soc. Sci. Bull.	Bulletin de la Société des Sciences Physiques et Naturelles de Toulouse
Trans. Acad. Sci. St. Louis	Transactions of the Academy of Sciences of St. Louis
Trans. Amer. Ceram. Soc.	Transactions of the American Ceramic Society
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society
Trans. Amer. Inst. Chem. Eng.	Transactions of the American Institute of Chemical Engineers
Trans. Amer. Inst. Homoeop.	Transactions of the American Institute of Homoeopathy, Philadelphia
Trans. Amer. Inst. Min. Eng.	Transactions of the American Institute of Mining Engineers
Trans. Amer. Med. Assoc. Sec. Pharm. Therap.	Transactions of the Section on Pharmacology and Therapeutics of the American Medical Association
Trans. Amer. Micro. Soc.	Transactions of the American Microscopical Society
Trans. Amer. Soc. Civ. Eng.	Transactions of the American Society of Civil Engineers
Trans. Cambr. Phil. Soc.	Transactions of the Cambridge Philosophical Society
Trans. Can. Inst.	Transactions of the Canadian Institute
Trans. Engl. Ceram. Soc.	Transactions of the English Ceramic Society
Trans. Faraday Soc.	Transactions of the Faraday Society
Trans. Geol. Soc. S. Africa	Transactions of the Geological Society of South Africa
Trans. Illum. Eng. Soc.	Transactions of the Illuminating Engineering Society
Trans. Inst. Brew.	Transactions of the Institute of Brewing
Trans. Jenner Inst. Prev. Med.	Transactions of the Jenner Institute of Preventive Medicine
Trans. Kansas Acad. Sci.	Transactions of the Kansas Academy of Science
Trans. Med.	Transactions Medicales; Journal de Medecine pratique
Trans. Min. Geol. Inst. India	Transactions of the Mining and Geological Institute of India
Trans. Natl. Eclec. Med. Assoc.	Transactions National Eclectic Medical Association Indianapolis
Trans. Nova Scotia Inst. Sci.	Transactions of the Nova Scotia Institute of Science
Transv. P.	Transvaal Patent
Trans. Path. Soc.	Transactions of the Pathological Society
Trans. Roy. Irish Acad.	Transactions of the Royal Irish Academy
Trans. Roy. Soc. Can.	Transactions of the Royal Society of Canada
Trans. Roy. Soc. Edinb.	Transactions of the Royal Society of Edinburgh
Trans. Roy. Soc. London	Transactions of the Royal Society of London
Trans. Soc. Engin.	Society of Engineers, Transactions
Trav. Com. Hyg. Publ.	Recueil des Travaux du Comite consultatif d'Hygiene Publique de France et des Actes Officiels de l'Administration Sanitaire
Trenton Natur. Hist. Soc. J.	Journal of the Trenton, New Jersey, Natural History Society
Treviso, Mem. Ateneo	Memorie Scientifiche e Litterarie dell' Ateneo di Treviso
Trier, Jahr.	Jahresbericht der Gesellschaft für nützliche Forschungen zu Trier
Triest Zool. Sta. Arb.	See Wien. Zool. Inst. Arb.
Trieste, Boll.	Bollettino della Societa Adriatica di Scienze Naturali in Trieste
Trieste Mus. Civ. Atti	Atti del Museo Civico di Storia Naturale di Trieste
Trieste, Program. Civ. Scuola	Programma della Civica Scuola Reale autonoma in Trieste

Trinidad Field Natur. Club J.	Journal of the Trinidad Field Nauralists' Club
Trinidad P.	Trinidad Patent
Trinidad, Proc. Sci. Assoc.	Proceedings of the Scientific Association of Trinidad
Trinidad, Sci. Assoc. Proc.	Proceedings of the Scientific Association of Trinidad
Trommsdorff, J. Pharm.	Journal der Pharmacie für Aerzte und Apotheker, und Chemiker
Tromso. Mus. Aarsh.	Tromso Museums Aarshefter
Tropenpflanzer	Tropenpflanzer (Der). Berlin
Tsch. Mineral. Mitth.	Tschermak's Mineralogische Mitteilungen
Tuberculosis	Tuberculosis. The Journal of the National Association for the Prevention of Consumption and other forms of Tuberculosis
Tübinger Blätter	Tübinger Blätter für Naturwissenschaften und Arzneikunde
Tübingen Bot. Inst. Unters.	Untersuchungen aus dem Botanischen Institut zu Tübingen
Tunis P.	Tunis Patent
Turin, Mem. Acad.	Memoires de l'Academie Royale des Sciences de Turin
Tyneside Natur. Field Club Trans.	Transactions of the Tyneside Naturalist's Field Club
U. K. Mar. Biol. Assoc. J.	Journal of the Marine Biological Association of the United Kingdom
U. S. Bur. Anim. Ind. Bull.	U. S. Department of Agriculture. Bureau of Animal Industry
U. S. Bur. Anim. Ind. Report	Annual Report of the Bureau of Animal Industry
U. S. Chief Signal Off. Ann. Report	Annual Report of the Chief Signal Officer (of the Army) to the Secretary of War
U. S. Coast Geod. Surv. Bull.	United States Coast and Geodetic Survey. Bulletin
U. S. Comm. Agric. Report	Report of the Commissioner of Agriculture
U. S. Dept. Agric. Bull.	Bulletins of the Department of Agriculture, U. S.
U. S. Dept. Agric. Report	Reports of the Department of Agriculture, U. S.
U. S. Dept. Agric. Yearb.	Yearbook of the United States Department of Agriculture
U. S. Disp.	United States Dispensatory
U. S. Div. Biol. Surv. Bull.	U. S. Department of Agriculture. Division of Biological Survey. Bulletin
U. S. Div. Chem. Bull.	U. S. Department of Agriculture. Division of Chemistry. Bulletin
U. S. Div. Entom. Bull.	U. S. Department of Agriculture. Division of Entomology
U. S. Div. Entom. Insect Life	U. S. Department of Agriculture. Division of Entomology. (Periodical Bulletin.) Insect Life
U. S. Div. Entom. Tech. Ser.	U. S. Department of Agriculture. Division of Entomology. Technical Series
U. S. Div. Ornith. Mamm. Bull.	U. S. Department of Agriculture. Division of Economic Ornithology and Mammalogy. Bulletin
U. S. Div. Soils Bull.	U. S. Department of Agriculture. Division of (Agricultural) Soils. Bulletin
U. S. Entom. Comm. Bull.	Department of the Interior...Bulletin of the United States Entomological Commission
U. S. Entom. Comm. Report	(U. S.) Department of the Interior (Agriculture)... Report of the United States Entomological Commission
U. S. Fish Comm. Bull.	Bulletin of the United States Fish Commission
U. S. Fish Comm. Report	United States Commission of Fish and Fisheries. Report of the Commissioner

U. S. Geol. Surv.	United States Geological Survey
U. S. Monthly Weath. Rev.	(United States) Monthly Weather Review
U. S. Mus. Bull.	Department of the Interior...Bulletin of the United States National Museum
U. S. Mus. Proc.	Department of the Interior...Proceedings of the United States National Museum
U. S. Mus. Report	See Smithsonian Rep.
U. S. Mus. Spec. Bull.	Smithsonian Institution. United States National Museum. Special Bulletin
U. S. Naval Inst. Proc.	United States Naval Institute Proceedings
U. S. Naval Med. Bull.	United States Naval Medical Bulletin
U. S. Naval Obs. Publ.	Publications of the United States Naval Observatory
U. S. N. Amer. Fauna	U. S. Department of Agriculture. Division of Ornithology and Mammalogy. North American Fauna
U. S. P.	United States Patent
U. S. Ph.	United States Pharmacopoeia
U. S. Secty. Agric. Report	Report of the secretary of agriculture
U. S. Signal Serv. Notes	United States of America: War Department. Signal Service Notes
U. S. Signal Serv. Pap.	United States of America, War Department. Professional Papers of the Signal Service
U. S. Surv. Terr. Reports	...Annual Report of the United States Geological (and Geographical) Survey of the Territories
U. S. Weath. Bur. Bull.	U. S. Department of Agriculture. Weather Bureau. Bulletin
U. S. Weath. Bur. Report	U. S. Department of Agriculture. Weather Bureau. Report of the Chief of the Weather Bureau
U. Serv. Inst. J.	Journal of the royal United Service Institution, Whitehall Yard
Udine, Relazioni	Relazioni intorno agli Atti dell' Accademia di Udine
Uhland's Tech. Rund.	Uhland's Technische Rundschau
Umschau	Umschau, Die
Ung. Naturwiss. Ver. Jahr.	Abhandlungen aus dem dritten Bande der Jahrbücher des Ungarischen naturwissenschaftlichen Vereins zu Pest, in Deutscher Uebersetzung Red. von J. Szabo
Univ. Ill. Bull.	University of Illinois Bulletin
Unters. Naturlehre	Untersuchungen zur Naturlehre des Menschen und der Thiere
Upsala, Arsskrift	Universitets Arsskrift utgifven af Kongl. Vetenskaps-Societeten i Upsala
Upsala Bot. För.	See Bot. Notiser
Upsala, Diss. Acad.	Dissertationes Academicae Upsaliae habitae
Upsala, Frey Tidskr.	Frey Tidskrift för Vetenskap och Konst
Upsala Läkareför. Förh.	Upsala Läkareförenings Förhandlingar
Upsala Naturvet. Studentsällsk.	See Bot. Centrbl.
Upsala, Soc. Sci. Nova Acta	Nova Acta Regiae Societatis Scientiarum Upsaliensis
Urug. P.	Uruguay Patent
Utrecht, Aanteek. Prov. Genoots.	Aanteekeningen van het Verhandelde in de Sectie-Vergaderingen van het Provinciaal Utrechtsch Genootschap van Kunsten en Wetenschappen
Utrecht, Ann. Acad.	Annales Academiae Rheno-Trajectinae
Utrecht, Kliniek	Kliniek: Tijdschrift voor Wetenschappenlijke Geneeskunde
Utrecht, Nieuwe Verh. Prov. Genootsch.	Nieuwe Verhandelingen van het Provinciaal Utrechsch Genootschap van Kunsten en Wetenschappen

Utrecht, Onderzoek.	Onderzoekingen gedaan in het Physiologisch Laboratorium der Utrechtsche Hoogeschool
Utrecht, Scheik. Onderzoek.	Scheikundige Onderzoekingen, gedaan in het Laboratorium der Utrechtsche Hoogeschool
Utrecht, Verh. Prov. Genootsch.	Verhandelingen van het Provinciaal Utregtsch Genootschap van Kunsten en Wetenschappen
Valais Soc. Murith.	See Bull. Murith.
Valencia, Act. Med.	Actas del Instituto Medico Valenciano
Valenciennes, Mem. Soc. Agric.	Memoires de la Société d'Agriculture, des Sciences, et des Arts, de l'Arrondissement de Valenciennes
Valentin, Rep.	Repertorium für Anatomie und Physiologie
Van Diemen's Land, Roy. Soc. Papers	Papers and Proceedings of the Royal Society of Van Diemen's Land
Van Diemen's Land, Roy. Soc. Reports	Reports of the Royal Society of Van Diemen's Land (For Horticulture, Botany, and the Advance of Science)
Van Nostrand's Mag.	Van Nostrand's Engineering Magazine
Vargasia	Vargasia: Boletin de la Sociedad de Ciencias fisicas y naturales de Caracas
Varsovie Soc. Natur. Trav.	Comptes Rendus et Memoires de la Société des Naturlistes (a l'Universite Imperiale) de Varsovie
Varsovie Soc. Natur. Trav. (Mem.)	Travaux de la Société des Naturalistes de l'Univsite Imperiale de Varsovie
Vaucluse Acad. Mem.	Memoires de l'Academie de Vaucluse
Venez. P.	Venezuela Patent
Venezia, Ateneo	L'Ateneo Veneto: Rivista mensile di Science, Lettere ed Arti
Venezia, Ateneo Esercit.	Esercitazioni Scientifiche e Letterarie dell' Ateneo di Venerzia
Venezia, Atti	Atti delle Adunanze dell' I. R. Istituto Veneto di Scienze, Lettere, ed Arti
Venezia, Atti Ateneo	Atti dell' Ateneo Veneto
Venezia, Iat. Atti	Atti del Reale Istituto Veneto di Scienze, Lettere ed Arti
Venezia, Ist Mem.	Memorie del Reale Istituto Veneto di Scienze, Lettere ed Arti
Venezia, Mem. Ist Beneto	Memorie dell' I. R. Istituto Veneto di Scienze, Lettere, ed Arti
Ver. Anal. Chem.	See Repert. Anal. Chem.
Verh. Genootsch. Occ. Qui Non.	Verhandelingen van het Genootschap: "Occidir qui qui non servat."
Verh. Ges. deut. Naturf. Aerzte	Verhandlung der Gesellschaft deutscher Naturforscher und Aerzte
Verh. poly. Ges.	Verhandlungen der poltechnischen Gesellschaft
Verh. Ver. Gewerbefleis.	Verhandlungen des Vereins zur Beförderung des Gewerbefleisses in Preussen
Veröffent. kais. Gesundh.	Veröffentlichungen des kaiserlichen Gesundheitsamts
Verona, Soc. Ital. Mem.	Memorie di Matematica e Fisica della Societa Italiana della Scienze
Vet. J. London	Veterinary Journal, London
Vet. Med. Assoc. Trans.	Transactions of the Veterinary Medical Association
Veterinarian	The Veterinarian
Victoria Dept. Mines Spec. Reports	Victoria. Department of Mines. Special Reports
Victoria Field Natur. Club	See Victorian Natlist.
Victoria Inst. J.	Journal of the Transactions of the Victoria Institute or Philosophical Society of Great Britain
Victoria Natur.	The Victorian Naturalist. The Journal and Magazine of the Field Naturalists' Club of Victoria

Victoria P.	Victoria Patent
Victoria Pharm. Soc. J.	Quarterly Journal and Transactions of the Pharmaceutical Society of Victoria
Victoria Proc. Roy. Soc.	Proceedings of the Royal Society of Victoria
Victoria Trans. Phil. Inst.	Transactions of the Philosophical Institute (afterwards Royal Society) of Victoria
Victoria Trans. Roy. Soc.	Transactions of the Royal Society of Victoria
Victoria Zool. Soc. Proc.	Proceedings of the Zoological and Acclimatisation Society of Victoria
Vierteljahrschr. ärzt. poly.	Vierteljahrschrift der ärztlichen Polytechnik
Vierteljahrschr. gericht. Med.	Vierteljahrschrift für gerichtliche Medizin und öffentliches Sanitatwesen
Vierteljahrschr. gesundheitspf.	Vierteljahrschrift für Gesundheitspflege
Vierteljahrschr. Zahnheilk.	Vierteljahrschrift für Zahnheilkunde
Virchow's Archiv path.	Virchows Archiv für pathologie, Anatomie, und Histologie
Viviani, Ann. Bot.	Annali di Botanica
Voget, Notizen	Notizen aus dem Gebeite der practischen Pharmacie
Voigt, Mag.	Magazin für den neuesten Zustand der Naturkunden, mit Rücksicht auf die dazu gehörigen Hülfswissenschaften
Vosges Soc. Emul. Ann.	Annales de la Société d'Émulation du Department des Vosges
W. Austral. P.	West Australian Patent
Wag. Free Inst. Sci. Trans.	Transactions of the Wagner Free Institute of Science of Philadelphia
Wag. Jahr.	(Wagner's) Jahresbericht über Chemische Technologie
Walker, Elect. Mag.	The Electrical Magazine
Warwick. Field Club Proc.	Proceedings of the Warwickshire Naturalists' and Archaeologists' Field Club
Warwick. Natur. Hist. Soc. Rep.	Annual Reports of the Warwickshire Natural History and Archaeological Society
Washburn Obs. Publ.	Publications of the Washburn Observatory of the University of Wisconsin
Washington	Int. Med. Congr. Trans., 1887
Washington	See also under U. S.
Washington Biol. Soc. Proc.	Proceedings of the Biological Society of Washington
Washington, Mem. Natl. Acad.	Memoirs of the National Academy of Sciences
Washington, Natl. Inst. Bull.	Bulletin of the Proceedings of the National Institution for the Promotion of Science
Washington Phil. Soc. Bull.	Bulletin of the Philosophical Society of Washington
Wasser Abwasser	Wasser und Abwasser
Water Supply Papers	Water Supply Papers
Watford Nat. Hist. Soc. Trans.	Transactions of the Watford Natural History Society and Hertfordshire Field Club
Weale, Quart. Papers	Quarterly Papers on Engineering
Weber, Archiv	Archiv für die systematische Naturgeschichte
Weimer, Zts. Geburtsk.	Gemeinsame Deutsche Zeitschrift für Geburtskunde
Weinlaube	Die Weinlaube
Wernigerode Naturwiss. Ver. Schr.	Schriften des Naturwissenschaftlichen Vereins des Harzes in Wernigerode
West. Brewer	Western Brewer, The
West. Chem. Met.	Western Chemist and Metallurgist
West. Drug.	Western Druggist

Westphäl, Prov. Blätt.	Westphälische Provincial-Blätter. Verhandlungen der Gesellschaft zur Beförderung der vaterländischen Cultur in Minden
Westphäl, Ver. Jahr.	Jahres-Bericht des Westfälichen Provinzial-Vereins für Wissenschaft und Kunst
Wetter	Das Wetter. Meteorologische Montasschrift für Gebildete aller Stände
Wetterau. Ges. Ann.	Annalen der Wetterauischen Gesellschaft für die gesammte Naturkunde
Wetterau. Ges. Festgabe.	Naturhistorische Abhandlungen aus dem Gebiete der Wetterau
Wetterau. Ges. Jahr.	Jahresbericht der Wetterauischen Gesellschaft für die gesammte Naturkunde
Wetterau. Ges. Naturk. Ber.	Bericht der Wetterauischen Gesellschaft für die gesammte Naturkunde zu Hanau
Wiad. Mat.	Wiadomosci Matematyczne
Wieck's Gewerbeztg.	Deutsche Gewerbezeitung (F. Wieck)
Wied. Ann. Phys.	Annalen der Physik und Chemie (Wiedemann's)
Wied. Archiv	Archiv für Zoologie und Zootomie
Wied. Zool. Mag.	Zoologisches Magazin
Wiegmann, Archiv	Archiv für Naturgeschichte
Wien Abh.	Naturwissenschaftliche Abhandlungen
Wien Akad. Ber.	Sitzungsberichte der kaiserlichen Akademie der Wissenschaften; Mathematisch-Naturwissenschaftliche Klasse, II Abthlg. Wien
Wien Akad. Denkschr.	Denkschriften der kaiserlichen Akademie der Wissenschaften. Mathematisch - Naturwissenschaftliche Classe
Wien Akad. Sitzber.	Sitzungsberichte der Mathematisch-Naturwissenschaftlichen Classe der kaiserlichen Akademie der Wissenschaften
Wien Almanach	Almanach der kaiserlichen Akademie der Wissenschaften
Wien Alpen-Verein, Jahr.	Jahrbuch des Oesterreichishcen Alpen-Vereins
Wien Anthrop. Ges. Mitth.	Mittheilungen der Anthropologischen Gesellschaft
Wien Anz.	Anzieger der kaiserlichen Akademie ker Wissenschaften: Math.-Naturwissensch. Classe
Wien Denkschr.	Denkschriften der Kaiselichen Akademie der Wissenschaften: Mathematisch - naturwissenschaftliche Classe
Wien Embryol. Inst. Mitth.	Mittheilungen aus dem Embryologischen Institute der k. k. Universität in Wien
Wien Geogr. Ges. Abh.	Abhandlungen der k. k. Geographischen Gesellschaft in Wien
Wien Geogr. Ges. Festschr.	Festschrift der k. k. Geographischen Gesellschaft 1884–1898
Wien Geogr. Ges. Mitth.	Mittheilungen der k. k. Geographischen Gesellschaft in Wien
Wien Med. Chir. Acad. Abh.	Abhandlungen der k. k. medicinisch-Chirurgischen Josephs-Academie zu Wien
Wien Med. Chir. Acad. Beob.	Beobachtungen der k. k. medicinisch-chirurgischen Josephs-Academie zu Wien
Wien Naturhist. Hofmus. Ann.	Annalen des k. k. Naturhistorischen Hofmuseums
Wien Ornith. Vrr. Mitth.	Mittheilungen des Ornithologischen Vereins in Wien
Wien Phot. Corresp.	Photographische Correspondenz. Organ der Photograph. Gesellsch. in Wien
Wien Schr.	Schriften des Vereines zur Verbreitung naturwissenschaftlicher Kenntnisse

Wien Sitzber.	Sitzungsberichte der Mathematisch-naturwissenschaftlichen Classe der Kaiserlichen Akademie der Wissenschaften
Wien, Sonnblick-Ver. Jahr.	Jahres-Bericht des Sonnblick-Vereines. Wien
Wien. technol. Blätter	Wiener technologishe Blätter
Wien Ver. Naturwiss. Kennt. Schr.	Schriften des Vereins zur Verbreitung Naturwissenschaftlicher Kenntnisse in Wien
Wien, Ver. Ges. Aerzte.	Verhandlungen der k. k. Gesellschaft der Aerzte zu Wien
Wien Verh. Gewerb-Vereins.	Verhandlungen des Neiderösterreichischen Gewerb-Vereins
Wien Wochenbl. Aerzte	Wochenblatt der k. k. Gesellschaft der Aerzte in Wien
Wien Zts. Ges. Aerzte	Zeitschrift der k. k. Gesellschaft der Aerzte zu Wien
Wien, Zool. Bot. Ges. Festschr.	Festschrift zur Feier des fünfundzwanzigjährigen Bestehens der k. k. Zoologisch-Botanischen Gesellschaft in Wien
Wien, Zool. Bot. Verh.	Verhandlungen der k. k. Zoologisch-Botanischen Gesellschaft in Wien
Wien, Zool. Inst. Arb.	Arbeiten aus dem Zoologischen Institute der Universität Wien ind der Zoologischen Station in Triest
Wiener Entom. Monatschr.	Wiener Entomologische Monatschrift
Wiener Entom. Ver. Jahr.	Jahresbericht des Wiener Entomologischen Vereins
Wiener Entom. Ztg.	Wiener Entomologische Zeitung
Wiener klin. Wochenschr.	Wiener klinische Wochenschrift
Wiener landw. Ztg.	Wiener landwirtschaftliche Zeitung
Wiener Med. Wochenschr.	Wiener medicinische Wochenschrift
Wiener Mitth. Phot.	Wiener Mitteilungen (Photographischen Inhalts)
Wiener Mus. Ann.	Annalen des Wiener Museums der Naturgeschichte
Wiener Poly. J.	Allgemeines Wiener polytechnisches Journal
Wiener Ztg.	Wiener Zeitung
Wiener Zts. Physik.	Zeitschrift für Physik, Chemie, und Mineralogie
Wild, Rep. Meteorol.	Repertorium für Meteorologie, herausg. von der kaiserlichen Akad. der Wissenschaften
Wilna, Collect. Med. Chir.	Collectanea medico-chirurgica Caesarea Academiae Medico-Chirurgicae cura edita
Wilts, Archaeol. Natur. Hist. Mag.	Magazine of the Archaeological and Natural History Society of Wiltshire
Wimereux Lab. (Stat.) Zool.	See Lille Inst. Zool. Trav.
Winchester, J. Sci. Soc.	Journal of Proceedings and Annual Reports of the Winchester and Hampshire Scientific and Literary Society
Wisconsin Acad. Trans.	Transactions of the Wisconsin Academy of Sciences, Arts, & Letters
Wisconsin Natur. Hist. Soc Bull.	Bulletin of the Wisconsin Natural History Society
Wisconsin Natur. Hist. Soc. Pap.	Occasional Papers of the Natural History Society of Wisconsin
Wisconsin Natur. Hist. Soc. Proc.	Proceedings of the Natural History Society of Wisconsin
Wisconsin Univ. Bull. Sci.	Bulletin of the University of Wisconsin. Science Series
Wiss. Abh. Phys.-Tech. Reichsanstalt	Wissenschaftliche Abhandlungen der Physikalish-Technischen Reichsanstalt
Wiss. Meeresuntersuch.	Wissenschaftliche Meeresuntesuchungen herausgegeben von der Kommission zur wissenschaftlichen Untersuchung der deutschen Meere in Kiel und der biologischen Anstalt auf Helgoland

Wochenbl. Archit. Ver.	Wochenblatt, herausgegeben von mitgliedern des Architekten-Vereins zu Berlin
Wochenbl. Papierfabr.	Wochenblatt der Papierfabriken
Wochensch. Brau.	Wochenschrift für Brauerei
Wochenschr. Centr.-Ver. Rubezuker-ind.	Wochenschrift des Central-Vereins für Rubenzuker-industrie in der Oesterr-Ung-Monarchie
Wochenschr. österr. Ing. Ver.	Wochenschrift des österreichischen Ingenieur und Architekten Vereins
Wochenschr. Ver. deut. Ing.	Wochenschrift des Vereins deutscher Ingenieure
Wollen-Gewerbe	Das Deutsche Wollen-Gewerbe
Wollen Ztg.	Wollen Zeitung
Wombat	The Wombat. The Journal of the Geelong Field Naturalists' Club, and the Gordon College Amateur Photographic Association
Woods Holl Mar. Biol. Lab. Bull.	Biological Bulletin. Edited by the Director and Members of the Staff, of the Marine Biological Laboratory, Woods Holl, Mass.
Woods Holl Mar. Biol. Lab. Lect.	Biological Lextures delivered at (from) the Marine Biological Laboratory (of) Woods Holl (Mass.)
Woolhope Field Club Trans.	Transactions of the Woolhope Naturalists' Field Club
Woolwich, Proc.	Minutes of Proceedings of the Royal Artillery Institution
World's Paper Trade Rev.	World's Paper Trade Review
Wunderlich, Archiv. Heilk.	See Roser und Wunderlich
Württemberg. Aerzt. Ver. Mitth.	Mittheilungen des Württembergischen Aerztlichen Vereins
Württemberg, Jahresh.	Jahreshefte des Vereins für vaterländische Naturkunde in Württemberg
Würzburg, Arb. Bot. Inst.	Arbeiten des Botanischen Instituts in Würzburg
Würzburg, Arb. Phys. Lab.	Arbeiten aus dem Physiologischen Laboratorium der Würzburger Hochschule
Würzburg. Med. Zts.	Würzburger medicinische Zeitschrift
Würzburg. Naturwiss. Zts.	Würzburger Naturwissenschaftliche Zeitschrift; Herausgegeben von der Physikalisch-Medicinischen Gesellschaft
Würzburg Phys. Med. Festschr.	Festschrift zur Feier ihres fünfzigjähreign Bestehens herausgegeben von der Physikalisch-Medizinischen Gesellschaft zu Würzburg
Würzburg, Phys. Med. Sitzber.	Sitzungsberichte der Physikalisch-Medicinischen Gesellschaft zu Würzburg
Würzburg, Phys. Med. Verh.	Verhandlungen der Physikalisch-Medicinischen Gesellschaft
Würzburg, Zool Inst. Arb.	Arbeiten aus dem Zoologisch-Zootomischen Institut in Würzburg
Year Book Pharm.	See Brit. Pharm. Confer. Proc.
Year-book of Pharm.	Year-book of Pharmacy
Yn Lioar Manninagh	Yn Lioar Manninagh. The Journal of the Isle of Man Natural History and Antiquarian Society
Yokohama, Mitth. Deut. Ges.	Mittheilungen der Deutschen Gesellschaft für Natur und Völkerkunde Ostasiens
Yonne	See Auxere
Yonne, Bull.	Bulletin de la Société des Sciences Historiques et Naturelles de l'Yonne
Yorksh. Natur. Union Trans.	The Transactions of the Yorkshire Naturalists' Union
Yorksh. Phil. Soc. Report	Annual Report of the Council of the Yorkshire Philosophical Society

Yorksh. Proc. Phil. Soc.	Proceedings of the Yorkshire Philosophical Society
Zach, Corresp.	Correspondence Astronomique, Geographique, Hydrographique, et Statistique
Zach, Monat. Corresp.	Monatliche Correspondenz zur Beförderung der Erd- und Himmels-Kunde
Zahntech.	Die Zahntechnische Reform
Zantedeschi, Ann. Fis.	Annali di Fisica
Zeeuwsch Genootsch. Nieuwe Verh.	Nieuwe Verhandelingen van het Zeeuwsch Genootschap der Wetenschappen
Zeeuwsch Genootsch. Wet. Archief	Archief Vroegere en Latere Mededeelingen voornamelijk in Betrekking tot Zeeland, uitgegeven door het Zeeuwsch Genootschap der Wetenschappen
Zentr. Biochem. Biophys.	Zentralblatt für Biochemie und Biophysik
Zentr. exp. Med.	Zentralblatt der experimentellen Medizin (former name Zentralblatt für die gesamte Physiologie und Pathologie des Stoffwechsels)
Zentr. inn. Med.	Zentralblatt für innere Medizin
Zentr. oesterr - ungar Papierind.	Zentralblatt für die oesterr-ungar Papierindustrie
Zentr. Physiol.	Zentralblatt für Physiologie
Zentr. Physiol. Path. Stoffwech.	Zentralblatt für die gesammte Physiologie und Pathologie des Stoffwechsels, Berlin und Wien
Zeuner, Civilingenieur	Der Civilingenieur, Zeitschrift für das Ingenieurwesen
Ziva	Živa: Casopis prirodnicky
Zool. Anz.	Zoologischer Anzeiger
Zool. Beitr.	Zoologische Beiträge
Zool. Bull.	Zoological Bulletin
Zool. Congr.	See Congr. Int. Zool. C. R. Int. Congr. Zool. Proc.
Zool. Jahr.	Zoologische Jahrbücher. Zeitschrift für Systematik, Geographie und Biologie der Thiere
Zool. J.	The Zoological Journal
Zool. Soc. Proc.	Proceedings of the Scientific Meetings (General Meetings for Scientific Business) of the Zoological Society of London
Zool. Soc. Trans.	Transactions of the Zoological Society of London
Zool. Vortr.	Zoologische Vorträge
Zoologica	Zoologica. Original-Abhandlungen aus dem Gesammtgebeite der Zoologie
Zoologist	The Zoologist; a monthly Journal of Natural History
Ztg. Blechind.	Illustrierte Zeitung für Blechindustrie
Zts. Akklimat.	Zeitschrift für Akklimatisation: Organ des Akklimatisations-Vereins in Berlin
Zts. allg. Erdkunde	Zeitschrift für allgemeine Erdkunde
Zts. allg. österr. Apoth.-Ver.	Zeitschrift des allgemeinen österreichischen Apotheker-Vereins
Zts. allg. Physiol.	Zeitschrift für allgemeine Physiologie
Zts. anal. Chem.	Zeitschrift für analytische Chemie
Zts. Anat.	Zeitschrift für Anatomie und Entwickelungsgeschichte
Zts. ang. Chem.	Zeitschrift für angewandte Chemie, und Zentralblatt für technische Chemie
Zts. ang. Mikr.	Zeitschrift für angewandte Mikroskopie mit besonderer Rücksicht auf die mikroskopischen Untersuchungen von Nahrungs- und Genussmitteln, technischen Produkten, Krankheitsstoffen, etc.
Zts. anorg. Chem.	Zeitschrift für anorganische Chemie
Zts. Bauwesen	Zeitschrift für Bauwesen
Zts. Berg-Hütten Salinenw.	Zeitschrift für das Berg-Hütten und Salinenwesen im Preussichen Staate
Zts. Biol.	Zeitschrift für Biologie

Zts. Bot.	Zeitschrift für Botanik
Zts. Chem.	Zeitschrift für Chemie
Zts. chem. Apparat.	Zeitschrift für chemische Apparatenkunde (Discontinued)
Zts. Chem. Ind.	Zeitschrift für die Chemische Industrie mit besonderer Berücksichtigung der chemisch-technischen Untersuchungsverfahren 1887; later Zts. ang. Chem.
Zts. chem. Ind. Kolloide	Zeitschrift für Chemie und Industrie der Kolloide
Zts. Chemotherap.	Zeitschrift für Chemotherapie und verwandte Gebiete. (formerly Folia Serologia)
Zts. deut. geol. Ges. Abh.	Zeitschrift der deutschen geologischen Gesellschaft Abhandlungen
Zts. deut. Landw.	Zeitschrift für deutsche Landwirthe
Zts. Dreschler	Zeitschrift für Dreschsler, Elfenbeingraveure und Holzbildhauer
Zts. Düngerw.	Zeitschrift für Düngerwesen
Zts. Electrochem.	Zeitschrift für Electrochemie
Zts. Entom. (Breslau)	Zeitschrift für Entomologie im Auftrage des Vereins für schlesische Insektenkunde zu Breslau
Zts. Ethnol.	Zeitschrift für Ethnologie
Zts. exper. Path. Therap.	Zeitschrift für experimentelle Pathologie und Therapie, Berlin
Zts. Farben-Ind.	Zeitschrift für Farben-Industrie
Zts. Feuerwehr.	Illustrirte Zeitschrift für die deutsche Feuerwehr
Zts. Fischerei	Zeitschrift für Fischerei
Zts. Fleisch. Milchhyg.	Zeitschrift für Fleisch- und Milchhygiene
Zts. Geburtsh.	Zeitschrift für Geburtshülfe und Frauenkrankheiten
Zts. Geburtsh. Gynäkol.	Zeitshrift für Geburtshülfe und Gynäkologie
Zts. ges. Brauw.	Illustrirte Zeitschrift das gesammte Brauwesen
Zts. ges. Getreidew.	Zeitschrift für das gesamte Getreidewesen
Zts. ges. Naturwiss.	Zeitshrift für die Gesammten Naturwissenschaften
Zts. Ges. Ornith.	Zeitschrift für die gesammte Ornithologie
Zts. ges. Textilind.	Zeitschrift für die gesamte Textilindustrie
Zts. ges. Wasserwirts.	Zeitschrift für die gesamte Wasserwirtschaft
Zts. Heilk.	Zeitschrift für Heilkunde, als Fortsetzung der Prager Vierteljahrsschrift für praktische Heilkunde
Zts. Hyg.	Zeitschrift für Hygiene und Infektionskrankheiten
Zts. Immunit. Abt. I. 13. Abt. Ref.	Zeitschrift für Immunitätsforschung und experimentelle. Therapie. Abteilung I. 13. Abteilung II. or Ref. 1 vol.
Zts. Induk. Abst. Vererbungslehre	Zeitschrift für Induktive Abstammungs- und Vererbungslehre
Zts. Instrumentenk.	Zeitschrift für Instrumentenkunde
Zts. Klin. Med.	Zeitschrift für Klinische Medizin
Zts. Krebsforsch.	Zeitschrift für Krebsforschung
Zts. Kryst. Mineral.	Zeitschrift für Krystallographie und Mineralogie
Zts. landw. Versuchsw.	Zeitschrift für das landwirtschaftliche Versuchswesen in Oesterreich
Zts. Malakozool.	Zeitschrift für Malakozoologie
Zts. Math. Phys.	Zeitschrift für Mathematik und Physik
Zts. math. Unterr.	Zeitschrift für mathematischen und naturwissenschaftlichen Unterrricht
Zts. Mikro. Tek.	Zeitschrift für Mikroscopischen Teknik.
Zts. Morphol. Anthrop.	Zeitschrift für Morphologie und Anthropologie
Zts. Nahr. Genuss. (Z. genuss)	Zeitschrift für Untersuchung der Nahrungs und Genussmittel, sowie der Gebrauchsgegenstände
Zts. Naturwiss.	Zeitschrift für Naturwissenshaften...im Auftrage (Organ) des Naturwissenschaftlichen Vereins für Sachsen und Thüringen

Zts. öffentl. Chem.	Zeitschrift für öffentliche Chemie
Zts. Ohrenheilk.	Zeitschrift für Ohrenheilkunde in deutscher und englischer Sprache
Zts. österr. Ing. Ver.	Zeitschrift des österreichischen Ingenieur und Architekten Vereins
Zts. paraf. Ind.	Zeitschrift für Parafin Industrie
Zts. Parasit.	Zeitschrift für Parasitenkunde
Zts. Pflanzenkrankheiten	Zeitschrift für Pflanzenkrankheiten
Zts. physik. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandschaftslehre
Zts. Physik. Chem. Unterr.	Zeitschrift für dem physikalischen und chemischen Unterricht
Zts. Physiol. Chem.	Zeitschrift für physiologische Chemie (Hoppe-Seylers)
Zts. prakt. Geol.	Zeitschrift für praktische Geologie
Zts. Psychol.	Zeitschrift für Psychologie und Physiologie der Sinnesorgane
Zts. ration. Med.	Zeitschrift für rationelle Medicin
Zts. Reprodukt.	Zeitschrift für Reproduktiontechnik
Zts. Rübenzuckerind.	Neue Zeitschrift für Rübenzuckerindustrie
Zts. Schiess Spreng.	Zeitschrift für das gesammte Schiess- und Sprengstoffwesen
Zts. Spiritusind.	Zeitschrift für Spiritusindustrie
Zts. Telegr. Ver.	Zeitschrift des deutsch-osterreichischen Telegraphen-Vereins
Zts. Thiermed.	Zeitschrift für Thiermedicin
Zts. Tuberkulose	Zeitschrift für Tuberkulose und Heilstättenwesen
Zts. Ver. deut. Ingen.	Zeitschrift des Vereins deutscher Ingenieure
Zts. Ver. Rübenzuckerind.	Zeitschrift des Vereins für die Rübenzucker-Industrie des deutschen Reichs
Zts. Ver. Zuckerind.	Zeitschrift des Vereins der deutschen Zuckerindustrie
Zts. Wiss. Geogr.	Zeitschrift für wissenschaftliche Geographie
Zts. wiss. Mikro.	Zeitschrift für wissenschaftliche Mikroscopie
Zts. wiss. Photochem.	Zeitschirft für wissenschaftliche Photographie, Photophysik, und Photochemie
Zts. wiss. Zool.	Zeitschrift für wissenschaftliche Zoologie
Zts. Zuckerind.	Zeitschrift für Zuckerindustrie
Zts. Zuckerind. Böhm.	Zeitschrift für Zuckerindustrie in Böhmen
Zürich Denkschr. Med. Chir. Ges.	Denkschrift der medizinisch-chirurgischen Gesellschaft des Kantons Zürich
Zürich Mitth.	Mittheilungen der Naturforschenden Gesellschaft in Zürich
Zürich, Monats.	Monatsschrift des wissenschaftlichen Vereins in Zürich
Zürich naturf. Ges.	Vierteljahrschrift der naturforschenden Gesellschaft in Zürich
Zürich Physik. Ges. Jahr.	...Jahresbericht der physikalischen Gesellschaft in Zürich
Zürich, Schweiz. Ges. Neue. Denkschr.	Neue Denkschriften der allgmeinen Schweizerischen Gesellschaft für die gesammten Naturwissenschaften
Zürich, Soc. Entom.	Societas Entomologica. Organ für den internationalen Entomologenverein. Zürich
Zürich, Unters. Physiol. Lab.	Untersuchungen aus dem Physiologischen Laboratorium der Züricher Hochschule
Zürich, Verh.	Verhandlungen der Medicinisch-chirurgischen Gesellschaft des Kanton Zürich im Jahr 1826
Zürich, Vierteljahrschr.	Vierteljahrsschrift der Naturforschenden Gesellschaft in Zürich
Zwickau Ver. Naturk. Jahr	Jahresbericht des Vereins für Naturkunde zu Zwickau
Zwolle, Vooruitgang.	De Vooruitgang; Tijdschrift voor Wetenschap

CHAPTER I.

CELLULOSE.[1]

COMPREHENSIVE knowledge of the nature, limitations and inner mechanics of cellulose esterification and etherification presupposes a thorough understanding of the substituent groups or aggregates entering into and comprizing those esters and ethers, including an intimate fundamental acquaintance with the various normal and modified celluloses and cognate carbohydrates—the predominating constituent of plant tissues, and the structural basis of the vegetable world.

Comparatively speaking, there are few substances more intricate in composition, complex in constitution, or ramified in

---

[1] For general information upon the subject of cellulose development, see T. Anderson, N. Ed. Phil. J. 1849, **47,** 132; J. prakt. Chem. 1849, **47,** 449; Jahr. Chem. 1849, **2,** 484. Barreswil and Rilliet, N. J. Pharm. **21,** 205; J. prakt. Chem. 1852, **56,** 334; abst. Jahr. Chem. 1852, **5,** 657. v. Baumhauer, Scheik. Onderzoek, **2,** 62, 194; abst. Ann. 1843, **48,** 356; J. prakt. Chem. 1844, **32,** 204, 210; N. Br. Arch. **53,** 68; Berz. Jahr. 1846, **25,** 585. A. Bechamp, Compt. rend. 1853, **37,** 134; 1856, **42,** 1210; Inst. 1853, 261; Ann. Chim. Phys. 1856, (3), **48,** 461; Ann. 1856, **100,** 367; J. prakt. Chem. 1856, **69,** 449; Jahr. Chem. 1856, **9,** 670, 674. Blondeau de Carolles, Rev. Sci. 1843, **14,** 476; abst. J. prakt. Chem. 1844, **32,** 427; Berz. Jahr. 1846, **25,** 582. Boettger, J. prakt. Chem. 1843, **30,** 257; Ann. 1843, **47,** 329; Berz. Jahr. 1845, **24,** 464. Braconnot, Ann. Chim. Phys. 1819, (2), **12,** 172; Schw. J. 1819, **27,** 328; Gilb. Ann. 1847, **63,** 347; abst. Berz. Jahr. 1822, **1,** 107. Chodnew, Ann. 1844, **51,** 393. C. Cramer, J. prakt. Chem. 1858, **73,** 1; abst. Chem. Centr. 1858, 50. P. Darnis, Dingl. Poly. 1855, **137,** 376; Mon. Ind. 1855, No. 1986; abst. Jahr. Chem. 1855, **8,** 901. L. de Koninck, Dingl. Poly. 1857, **144,** 359; Rev. univ. 1857, 131; abst. Jahr. Chem. 1857, **10,** 648. Dullo, Dingl. Poly. 1860, **158,** 392; Chem. Centr. 1860, 25; abst. Jahr. Chem. 1860, **13,** 715; J. Emmet (Sill.), Am. Jour. Sci. 1837, **32,** 140; J. prakt. Chem. 1837, **12,** 120; abst. Berz. Jahr. 1839, **18,** 275. O. Erdmann and M. Mittenzwey, J. prakt. Chem. 1859, **76,** 386; Chem. Centr. 1859, 642; abst. Jahr. Chem. 1859, **12,** 541. A. Franchimont, Compt. rend. 1879, **89,** 711, 713, 755; Ber. 1879, **12,** 1939; abst. Jahr. Chem. 1879, 832. E. Fremy, Compt. rend. 1859, **48,** 202; N. J. Pharm. **35,** 81; abst. Rep. Chim. Pure, 1859, **1,** 269; Compt. rend. 1859, **48,** 325, 360, 667, 862; J. Pharm. **35,** 321, 401; abst. Inst. 1859, 121, 151; Rep. Chim. Pure, 1859, **1,** 357, 433; Pharm. Vierteljahr. **9,** 221. N. J. Pharm. Inst. 1859, 357; Rep. Chim. Pure, 1859, **1,** 602; Chem. Centr. 1860, 4. Compt. rend. 1859, **49,** 561; Jahr. Chem. 1859, **12,** 529, 530, 532, 533, 534, 537, 540. E. Fremy and Terreil, J. Pharm. Chim. 1868, **7,** 241; Chem. Centr. 1868, 616; abst. Jahr. Chem. 1868, 762. Fromberg, Scheik. Onderzoek, **2,** 36; abst. Ann. 1843, **48,** 353; J. prakt. Chem. 1844, **32,** 198; Mulder, Physiol. Chem. 1844,

reactivity, or about which it is more difficult to arrive at tangible, definite conclusions than with the celluloses. This is partially accountable from the fact that what we call "cellulose" is not the distinctive name of a definitely characterized chemical individual, but rather the collective name of a closely interrelated series of allied members, which often by imperceptible gradations merge one into another.

Their ready susceptibility to oxidation and reduction; hydrolysis and dehydration; condensation and depolymerization; either before, during or after alkylation or acidylation, thus

---

198; Berz. Jahr. 1845, **24**, 462. Fourcroy, Systeme des Connaissances chimiques, **8**, 87. J. Gladstone, Mem. Chem. Soc. 1850, **3**, 412. E. Gilson, La Cellule, 1893, **9**, 397; abst. J. C. S. 1894, **66**, i, 107; Chem. Centr. 1893, II, 530; Jahr. organ. Chem. 1893, **1**, 265; J. S. C. I. 1894, **13**, 1106; Bull. Soc. Chim. 1894, **11**, 590; Jahr. Chem. 1893, 881. Gay-Lussac, Ann. Chim. Phys. 1829, (2), **41**, 398; Pogg. Ann. 1829, **17**, 171; Schw. J. 1830, **58**, 87; abst. Berz. Jahr. 1831, **10**, 183. Gmelin, Schw. J. 1830, **58**, 374, 377. W. Henneberg, Ann. 1868, **146**, 130; abst. Bull. Soc. Chim. 1868, (2), **10**, 414; Jahr. Chem. 1868, 761. Compare Ritter, Jahr. Chem. 1868, 761. Harting, Scheik. Onderzoek. **3**, 17; abst. Berz. Jahr. 1847, **26**, 613; J. prakt. Chem. 1846, **37**, 329; Annuaire de Chim. 1847, 606. W. Hoffmeister, Landw. Versuchstat. 1886, **33**, 153; abst. Jahr. Chem. 1886, 2103; 1891, **39**, 461; 1897, **48**, 401; 1901, **55**, 115; Landw. Jahr. 1888, **17**, 239; 1889, **18**, 767; J. C. S. 1886, **50**, 954; 1890, **58**, 581; 1892, **62**, 129; 1898, **74**, ii, 148, 544; 1901, **80**, ii, 205; Ber. 1893, **26**, R, 497; Jahr. Chem. 1898, 1368; 1901, 889; Chem. Centr. 1890, I, 112; 1897, I, 1004; 1901, I, 862; J. S. C. I. 1897, **16**, 940. Hermann, J. prakt. Chem. 1841, **23**, 380; 1842, **27**, 165; abst. Berz. Jahr. 1843, **22**, 499; 1844, **23**, 315. Johnson, Bot. Gaz. 1895, **20**, 16. John, Chem. Schriften, **4**, 204. G. Kindt, Dingl. Poly. 1846, **102**, 334; 1847, **105**, 189; Chem. Centr. 1865, 320; Ann. 1847, **61**, 253; Phil. Mag. 1847, (3), **31**, 157; J. Pharm. (3), **11**, 324; Jahr. Chem. 1847–8, **1**, 1122. F. Koch, Pharm. Zts. Russ. **25**, 619, 635, 651, 667, 683, 699, 730, 747, 763; abst. Ber. 1887, **20**, 145. W. Kirchner and B. Tollens, Ann. 1875, **175**, 221; abst. J. C. S. 1875, **28**, 1179; Jahr. Chem. 1875, 799; Jahr. rein Chem. 1875, **3**, 381. H. Kopp, Ann. 1840, **35**, 39. Mitscherlich, Berl. Akad. Ber. 1850, 102; Ann. 1850, **75**, 305; J. prakt. Chem. 1850, **50**, 144; abst. Pharm. Centr. 1850, 385; Chem. Gaz. 1851, 61; Instit. 1850, 228; Jahr. Chem. 1850, **3**, 541. H. v. Mohl, Flora, 1840; Vermischte Schriften, 1845, 335; Bot. Ztg. 1847, 497. A. Morin, Ann. Chim. Phys. 1832, (2), **49**, 311; Bull. univers. **50**, 337; Schw. J. **66**, 362; abst. Berz. Jahr. 1834, **13**, 77. G. Mulder, Scheik. Onderzoek. **2**, 76; abst. J. prakt. Chem. 1844, **32**, 336; Ann. 1841, **39**, 150. A. Müntz, Compt. rend. 1882, **94**, 453; abst. Jahr. Chem. 1882, 1151; Bull. Soc. Chim. 1882, (2), **37**, 409; Ber. 1882, **15**, 937; J. C. S. 1882, **42**, 707; Chem. News, 1882, **45**, 99. Compt. rend. 1886, **102**, 624, 681; abst. J. C. S. 1886, **50**, 575; Bull. Soc. Chim. 1886, (2), **46**, 486; Ber. 1886, **19**, 299; J. S. C. I. 1886, **5**, 386; Chem. News, 1886, **53**, 167, 180; Jahr. Chem. 1886, 1809. A. Payen, N. Ann. Sc. Nat. Bot. 1839, **11**, 21, 27; **14**, 37; Compt. rend. 1840, **10**, 941; 1844, **18**, 271; 1859, **48**, 210, 275, 319, 326, 328, 358, 362, 772, 893; abst. Rep. Chim. Pure, 1859, **1**, 270, 359, 434; N. J. Pharm. **35**, 88, 185. Jahr. Chem. 1859, **12**, 530, 531, 532, 533, 534, 536, 539; Ann. Sc. Nat. 1839, (2), **2**, 21; 1840, (2), **3**, 73. E. Peligot, Compt. rend. 1839, **9**, 135; 1858, **47**, 1037; abst. Berz. Jahr. 1841, **20**, 541; abst. Jahr. Chem. 1858, **11**, 574. See also C. Gerhardt, Ann. Chim. Phys. 1839, (2), **72**, 208, (Cuprammonium). J. Pelouze, giving rise to an indeterminate number of products often similar in appearance, analogous in properties yet differing from the original cellulose, only complicates the subject. Especially is this true, where the elementary composition remains the same and the chemical changes are analytically indistinguishable.

All plant tissues—from the minute unicellular organism to the giant conifers of California—are comprised of cells, and the envelope or investing matrix of these cells is composed of cellulose. In the higher plants the individual cells co-apt and coalesce in such a manner that their walls are broken up with the formation of

Compt. rend. 1859, **48**, 210, 327; N. J. Pharm. **35**, 88; Rep. Chim. Pure, 1859’ **1**, 272; Dingl. Poly. 1859, **151**, 394; Jahr. Chem. 1859, **12**, 532. A. Poggiale’ N. J. Pharm. **36**, 121; Compt. rend. 1859, **49**, 128; abst. Rep. Chim. Pure, 1859, **1**, 521; Chem. Centr. 1859, 844; Jahr. Chem. 1859, **12**, 733. J. Porter, Ann. 1849, **71**, 115; Am. J. Sci. (Sill.) 1850, (2), **9**, 20; abst. Pharm. Centr 1849, 777; Chem. Gaz. 1849, 469; Jahr. Chem. 1849, **2**, 474. L. Pozzoz, Compt. rend. 1858, **47**, 207; J. prakt. Chem. 1859, **76**, 314; abst. Jahr. Chem. 1858, 242. J. Poumarede and O. Figuier, Memoire sur le Ligneux, etc. Paris, 1847; N. J. Pharm. **11**, 458; **12**, 81; J. prakt. Chem. 1847, **42**, 25; Compt. rend. 1846, **23**, 918; 1847, **25**, 17; Ann. 1847, **64**, 387; Repert. Pharm. (2), **47**, 344; Jahr. Chem. 1847–8, **1**, 795, 797. J. Proust, J. Phys. **48**, 469; Schw. J. **7**, 707. L. Radikofer, Ann. 1855, **94**, 332; abst. J. prakt. Chem. 1855, **66**, 127; Pharm. Centr. 1855, **26**, 566; Dingl. Poly. 1855, **138**, 152; Jahr. Chem. 1855, **8**, 821. T. Ransome, Phil. Mag. 1887, **30**, 4. J. Reade, Lon. Ed. Phil. Mag. 1837, **11**, 421. H. Reinsch, Jahr. Pr. Pharm. **14**, 25; Dingl. Poly. 1860, **156**, 156; Chem. Centr. 1860, 491; Bayer. Gewerbeztg. 1860, No. 8; Jahr. Chem. 1859, **12**, 746. R. Reiss, Ber. 1889; **22**, 609; Jahr. Chem. 1889, 2086; 1890, 2183. Landw. Jahr. 1889, **18**, 707; Chem. Centr. 1889, I, 541; 1890, I, 165; Bot. **7**, 322; J. S. C. I. 1889, **8**, 406; J. C. S. 1889, **56**, 687; 1891, **60**, 365; Bull. Soc. Chim. 1890, (3), **3**, 713; Rev. gén. Sci. 1890, **1**, 244. F. Rochleder and W. Heldt, Ann. 1843, **48**, 8; abst. Berz. Jahr. 1845, **24**, 382; J. Pharm. 1844, **5**, 89. F. Rochleder, Ann. 1844, **50**, 225; abst. Berz. Jahr. 1846, **25**, 864; Ann. 1846, **59**, 300; 1847, **63**, 193; J. prakt. Chem. 1846, **39**, 367; J. Pharm. 1844, **6**, 161; 1848, **14**, 445. J. Rossignon, Compt. rend. 1842, **14**, 873; B. Rumford, Schw. J. **8**, 160. F. Sacc, Ann. Chim. Phys. 1849, (3), **25**, 218; J. prakt. Chem. 1849, **46**, 430; Pharm. Centr. 1849, 235; Chem. Gaz. 1849, 274; Jahr. Chem. 1849, **2**, 473. N. Saussure, N. Allg. J. Chem. (Gehl.) 1804, **4**, 681. Ann. Chim. Phys. 1804, **50**, 225; Ann. Phys. (Gilb.) 1804, **18**, 208; J. de Phys. 1804, **58**, 393; Phil. Mag. 1805, **20**, 307. Schaefer, Ann. 1871, **160**, 312; abst. Jahr. Chem. 1871, 789; Bull. Soc. Chim. 1872, **17**, 371; J. C. S. 1872, **25**, 309. J. Schlossberger, Ann. 1858, **107**, 22; J. prakt. Chem. 1858, **73**, 370; N. Br. Arch. **95**, 145; Ann. 1859, **110**, 246; N. Jahr. Pharm. **12**, 6; abst. J. prakt. Chem. 1859, **77**, 508; Rep. Chim. Pure, 1859, **1**, 432; Chem. Centr. 1858, 474; Jahr. Chem. 1858, **11**, 199; J. prakt. Chem. 1859, **78**, 370; abst. Rep. Chim. Pure, 1860, **2**, 142; Jahr. Chem. 1859, **12**, 542; see also J. prakt. Chem. 1859, **78**, 372. J. Schrader, Schw. J. **33**, 410. E. Schweizer, Chem. Centr. 1858, 49; J. prakt. Chem. 1857, **72**, 109; 1859, **78**, 370; Rep. Chim. Pure, 1860, **2**, 142; Vierteljahrsch. Zürich. naturforsch. Gess., abst. Dingl. Poly. 1857, **146**, 361; Jahr. Chem. 1857, **10**, 246. M. Schleiden, Berz. Jahr. 1841, **20**, 342; Wiegm. Arch. 1838, 59; Pogg. Ann. 1838, **43**, 391; Grundz. d. wissensch. Botanik, Leipzig, 1849, **1**, 172; Ann. 1836, **17**, 139; 1839, **30**, 2660; 1842, **42**, 306; Flora, 1842, 237. J. Schlossberger and O. Doeptubular structures, which often attain extraordinary lengths—i. e., several hundred times their diameter.

Carbohydrates are a widely distributed and numerous class of bodies, found in the vegetable kingdom primarily, although carbohydrates of animal origin are not unknown. Strictly speaking, they contain six or a multiple of six carbon atoms, and from the fact that they always contain carbon, and the ratio of the hydrogen and oxygen atoms is the same as in water, accounts for their name.

The carbohydrates form the basis of alcoholic drinks and

ping, Ann. 1844, **52**, 113; abst. Berz. Jahr. 1846, **25**, 588; Annuaire Chim. 1846, 636. E. Schmidt and Hecker, J. prakt. Chem. 1847, **40**, 257; abst. Jahr. Chem. 1847–8, **1**, 1130; Poly. Centr. 1847, 36. F. Schulze, Beiträge zur Kenntniss des Lignins, Rostock, 1856; abst. Chem. Centr. 1857, 321; Jahr. Chem. 1855, 702, 1019. E. Schulze and E. Steiger, Ber. 1887, **20**, 290; abst. Jahr. Chem. 1887, 2270; Bull. Soc. Chim. 1887, **48**, 280. J. C. S. 1887, **52**, 460; Chem. News, 1889, **59**, 377; J. S. C. I. 1887, **6**, 446. C. Schmidt, J. prakt. Chem. 1846, **38**, 433. L. Schaffner, Ann. 1844, **50**, 148; abst. Berz. Jahr. 1846, **25**, 586. P. Schuetzenberger, Zts. Chem. Pharm. 1861, **4**, 65; abst. Bull. Soc. Chim. 1861, (1), **3**, 16. P. Thenard, Compt. rend. 1861, **52**, 444; Rep. Chim. Pure, 1861, **3**, 207; Bull. Soc. Chim. 1861, (1), **3**, 33; Jahr. Chem. 1861, **14**, 908; Chem. News, 1861, **4**, 136. G. Staedeler, Ann. 1859, **111**, 27; J. prakt. Chem. 1859, **78**, 169; Chem. Centr. 1859, 705; J. Pharm. (3), **36**, 229; Rep. Chim. Pure, 1859, **1**, 569; Jahr. Chem. 1859, **12**, 598. J. Stenhouse, Phil. Mag. 1841, **18**, 122; Ann. 1840, **35**, 301. J. Thomson, Ann. 1849, **69**, 128; J. prakt. Chem. 1840, **19**, 146; Phil. Mag. 1834, **5**, 355. L. Vauquelin, Schw. J. **12**, 2530. F. Versmann and A. Oppenheim, Pharm. J. Trans. (2), **1**, 385, 422; Chem. News, 1860, **1**, 20; Jahr. Chem. 1860, **13**, 715; Br. Assoc. Rep. No. 29, 86; J. prakt. Chem. 1860, **80**, 433; Dingl. Poly. 1860, **158**, 66; Zts. Chem. Pharm. 1860, 240; see also Dingl. Poly. 1860, **156**, 157; abst. Chem. Centr. 1860, 352; Rep. Chim. Appl. 1860, **2**, 59. M. Vincent, Compt. rend. 1847, **24**, 542; abst. Pharm. Centr. 1848, 500; Jahr. Chem. 1847-8, **1**, 1122; see also Gaudichaud, Boussingault and Payen; Compt. rend. 1849, **29**, 491; abst. Instit. 1849, 353; Mon. ind. 1849, No. 1397; Dingl. Poly. 1850, **115**, 150; Pharm. Centr. 1849, 909; Jahr. Chem. 1849, **2**, 711. Weiss, Chem. Centr. 1871, 179; Mon. Sci. 1869, **11**, 342; 1870, **12**, 23; Bull. Soc. Chim. 1870, **13**, 93; Jahr. Chem. 1869, 1103. H. Weber, Pharm. Viertelj, **7**, 538; Pharm. Centr. 1858, 864; Jahr. Chem. 1858, **11**, 577. E. Winterstein, Ber. 1893, **26**, 362; abst. Chem. Centr. 1893, I, 602; Jahr. organ. Chem. 1893, **1**, 266; Zts. Physiol. Chem. 1893, **18**, 43; Bull. Soc. Chim. 1893, **10**, 699; J. C. S. 1893, **64**, i, 380, 497; Meyer Jahr. Chem. 1893, **3**, 236; J. S. C. I. 1893, **12**, 702. F. Winkler, J. prakt. Chem. 1839, **17**, 65. Bachet, Jahr. Chem. 1866, 663. N. Basset, Belg. P. 138952, 1898. J. Batka, Chem. Centr. 1859, 865; abst. Poly. Notiz. 1860, **15**, 3; Dingl. Poly. 1859, **154**, 395; Vierteljarhsch. Pharm. **9**, 275; Rep. Chim. Pure, 1860, **2**, 142; Jahr. Chem. 1859, **12**, 543. E. von Baumhauer and P. Fromberg, Ann. 1843, **48**, 356; J. prakt. Chem. 1844, **32**, 204. Chem. Gazz. 1847, **5**, 413; J. prakt. Chem., 1844, 32, 210. A. Baeyer, Ber. 1869, **2**, 54; abst. Bull. Soc. Chim. 1869, **12**, 292. F. Bayer & Co. Belg. P. 226582, 1910; F. Beltzer Rev. gen. Chim. 1910, **13**, 20; abst. Chem. Zentr. 1910, I, 1596; C. A. 1910, **4**, 1369. C. Beadle, J. Frank. Inst. 1894, **138**, 100; abst. Jahr. Chem. 1894, 1134; Chem. Trade J. 1894, 128; J. S. C. I. 1894, **13**, 900. J. Beggaard and B. Gottschalk, Norw. P. 20847, 1909. R. Boettger, Chem. Centr. 1874, 309; Dingl.

the majority of foodstuffs, starch being the chief ingredient of flour, from which bread is made. Cellulose, related to it, is of interest in this work from the fact that organic and inorganic esters may be prepared therefrom, of increasing interest both in the peaceful and warlike arts.

According to the older system of carbohydrate classification three groups were recognized, one containing isomeric

Poly. 1874, **213**, 362; Jahr. phys. Ver. Frankfurt, 1872–73, 70; Zts. anal. Chem. 1874, **11**, 246; Jahr. Chem. 1874, 1031. A. Colassi, Caout. Guttap. 1918, **15**, 9604; abst. J. S. C. I. 1918, **37**, 686-A. T. Chaudhuri, Modern Chemistry and Chemical Industry of Starch and Cellulose, 156 pages. C. Cross and E. Bevan, J. Soc. Arts, 1896-7, **45**, 225, 684, 703,715; Proc. U. S. Nav. Inst. 1886, **12**, 624; Chem. News, 1889, **60**, 163, 254; abst. Chem. Centr. 1889, II, 790; 1890, I, 21; Jahr. Chem. 1889, 2066; 1890, 2152. J. C. S. 1890, **57**, 1. Compagnie Industrielle des alcools de l'Ardeche, Swiss P. 53961, 1910; A. Deiss, Span. P. 47327, 1910; Port. P. 7164, 1910. A. Deiss and C. Fournier, Aust. P. Anm. 6861, 1909. K. Duncan, Sci. Amer. Suppl. Apr. 28, 1900. E. Durin, Ber. 1876, **9**, 1430, 1446; Compt. rend. 1876, **83**, 128; abst. Chem. News, 1876, **34**, 63; J. C. S. 1877, **31**, 106; Jahr. Chem. 1876, 947. E. Jandrier, Schw. Wochensch. f. Pharm. u. Chem. 1899, 489; abst. Amer. J. Pharm. 1900, **72**, 497; Compt. rend. 1899, **128**, 1407; Chem. Centr. 1899, II, 184; Bull. Soc. Chim. 1899, (3), **21**, 895; Jahr. Chem. 1899, 1295, 1297; J. A. C. S. 1899, **21**, 1175; J. C. S. 1899, **76**, i, 788; 1900, **78**, ii, 177; Chem. News, 1899, **80**, 11. C. Kellner, U. S. P. 773941, 1904; abst. J. S. C. I. 1904, **23**, 1159; F. P. 326313, 1902, abst. J. S. C. I. 1903, **22**, 817, 1304; Mon. Sci. 1904, **61**, 46. A. Klein, Papier Ztg. **31**, 4286; Chem. Ztg. 1906, **30**, 1259; abst. C. A. 1907, **1**, 485, 2492; Wochenbl. Papierfabr. **38**, 1813; Zts. ang. Chem. 1907, **20**, 610; Bull. Soc. Chim. 1907, (4), **2**, 905; Chem. Centr. 1907, I, 381. W. Massot, Zts. ang. Chem. 1909, **22**, 241, 299; 1911, **24**, 433; abst. Kunst. 1911, **1**, 452; Chem. Zentr. 1909, I, 801; 1911, I, 1259; C. A. 1910, **4**, 1240; 1911, **5**, 1995. P. Marino, Ital. P. 302/5/101627, 1909. P. Michela, Ital. P. 30024, 1892. H. Mork, J. Frank. Inst. 1917, **184**, 353; abst. C. A. 1917, **11**, 3430. A. Sander, Fortschritte Chem. **4**, 293; abst. C. A. 1912, **6**, 153. C. Schwalbe, Chem. Zts. 1908, **32**, 287; abst. J. C. S. 1908, **94**, i, 250, 321; Mon. Sci. 1910, **72**, 825; J. Frank. Inst. **170**, 371; Papier Ztg. **36**, 2496, 2531, 2667, 2699, 2735, 2769; abst. C. A. 1911, **5**, 3908; Papier Ztg. **36**, 2599, 2631; abst. C. A. 1911, **5**, 3729; Papier Ztg. **39**, 2486, 2543; abst. C. A. 1915, **9**, 713. J. Schmitt, F. P. 377979, 1907; abst. J. S. C. I. 1907, **26**, 1088; Mon. Sci. 1908, **69**, 29; C. A. 1908, **2**, 1368. F. Schulz, Zts. physiol. Chem. 1900, **29**, 124; abst. J. C. S. 1900, **78**, ii, 292; Chem. Centr. 1900, I, 729; Bull. Soc. Chim. 1901, **26**, 32. Societe Thirion et Bonnet, F. P. 308446, 1901. W. Walker, Mon. Sci. 1908, **69**, 461; J. Frank. Inst. 1907, **164**, 131; abst. C. A. 1908, **2**, 318, 2619. W. Whitney, U. S. P. 923745; abst. J. S. C. I. 1909, **28**, 743; see also U. S. P. 923227; abst. J. S. C. I. 1909, **28**, 743; C. A. 1909, **3**, 2091. Wichelhaus, Inter. Cong. London, abst. Zts. ang. Chem. 1909, **22**, 1119. Ber. 1910, **43**, 2922; abst. J. S. C. I. 1910, **29**, 1369; Chem. Zentr. 1910, II, 1961; J. C. S. 1910, **98**, i, 868; Meyer Jahr. Chem. 1910, **20**, 317; Bull. Soc. Chim. 1911, (4), **10**, 1054; C. A. 1911, **5**, 2953; Rep. Chim. Appl. 1911, **11**, 138. W. Vieweg, Wochenblatt für Papierfabrikation, 1911, 3541, 3729; abst. Kunst. 1911, **1**, 452; C. A. 1911, **5**, 3907. Papier Ztg. 1907, **32**, 309, 398; Chem. Ztg. 1907, **31**, 85; Chem. Zentr. 1907, I, 677; C. A. 1907, **1**, 1319. E. Vitrebert, Papier, 1914, **17**, 134; abst. C. A. 1915, **9**, 148. Worlds Paper Tr. Rev. **67**, No. 8, p. 32; No. 12, p. 22. See Caout. et Guttap. 1919, **16**, 9888; C. A. 1919, **13**, 3314.

compounds of the type $C_6H_{12}O_6$ termed the glucose or grape sugar group; a second containing compounds of the formula $C_{12}H_{22}O_{11}$ and designated as the saccharose or cane-sugar group; while a third division was made of the highly complex, cryptocrystalline or amorphous compounds, to which starch and cellulose are types. This classification, although inadequate is still retained, the word "glucose" being now reserved for the dextro and laevo enantiomorphs of grape sugar to take the place of the older word "dextrose," which became unsuitable after the discovery of the laevo enantiomorphic form. As a comprehensive classification, the three older groups of carbohydrates may be distinguished by the names:

Monosaccharoses, Monosaccharides, Monoses (formerly glucoses).

Disaccharoses, Disaccharides, Saccharobioses (formerly saccharoses).

Polysaccharoses, Polysaccharides (formerly amyloses).

After E. Fischer had succeeded in synthesizing a number of new sugars containing more or less than six carbon atoms, a further subdivision of the monosaccharoses became necessary. Many new compounds were synthesized, containing two to nine carbon atoms and possessing the general characteristics of the monosaccharoses, and being distinguished by the names biose, triose, tetrose, etc. Inasmuch as some of the monosaccharoses combine the properties of alcohol and aldehydes, while others partake of the properties of alcohols and ketones, the further distinction of "aldose" and "ketose" has been necessary.

Tollens[1] has devised the following comprehensive scheme of classification of the carbohydrates:

I. Monosaccharides (Glycoses).
    (a) Monose, Formaldehyde.
    (b) Diose, Glycolaldehyde, Glycolose.
    (c) Triose, Aldotriose (Glycerose), Ketotriose (Dioxyacetone).
    (d) Methyltriose, Methylglycerolaldehyde.

---

[1] "Kurtz Lehrbuch der Kohlenhydrate," 1914. E. v. Lippmann, "Die Chemie der Zuckerarten," 1904. L. Macquenne, "Les Sucres et leurs principaux derives," 1900. E. Armstrong, "The Simple Carbohydrates," 1910. E. Fischer, "Untersuchungen ueber Kohlenhydrate 1884–1908," 1909.

- (e) Tetrose, Aldotetrose (Erythrose), Ketotetrose (Erythrulose).
- (f) Pentose, Arabinose, Xylose, Ribose.
- (g) Methylpentose, Rhamnose, Rhodeose, Fucose.
- (h) Hexose, Glucose, Mannose, Galactose, Fructose, Sorbose.
- (i) Glycose with 7 carbon atoms, Rhamnohexose.
- (j) Glycose with 8 carbon atoms, Rhamnoheptose, Mannooctose.
- (k) Glycose with 9 carbon atoms, Rhamnooctose, Mannononose.
- (l) Glycose with 10 carbon atoms, Glucodecose.

II. Di- and Poly-saccharides.
- (a) Disaccharide, Arabiose, Saccharose, Maltose, Cellose, Lactose.
- (b) Trisaccharide, Rhamnotriose, Raffinose, Melezitose, Triamylose.
- (c) Tetrasaccharide, Lupeose, Stachyose, Manneotetrose.

III. Polysaccharide (Saccharo-colloids).
- (a) Pentosan-colloids, Araban, Xylan.
- (b) Arabin, Tragacanth, Bassorin, Pectins.
- (c) Starch, Dextran, Glycogen, Hemicellulose, Amyloid, Lichenin.
- (d) Paramanan, Seminin.
- (e) Gelactan, Gelose, Gelan.
- (f) Levulosin, Fructosan, Inulin, Asparagose.
- (g) Glucosamine.
- (h) Cellulose, Hydrocellulose, Oxycellulose, Cellulose Esters.

In general, the molecular magnitude is the basis of arrangement of these polyhydroxy-aldehydes and ketones, and to the substances which give these when hydrolyzed by heating with mineral acids.

Nearly all of the naturally occurring carbohydrates are optically active, the specific rotatory power being influenced not only by the temperature and concentration of their solutions, but also not infrequently by the presence of optically inactive bodies.[1] Some representatives also exhibit the phenomena of birotation and semirotation. By heating the solutions for a brief period, constant rotation is usually obtained. The determination of the rotatory power of the carbohydrates by means of the saccharometer, not only ascertains their purity, but may be made quantitative.

As to their general characteristics. The members may be either soluble or insoluble, in water, those soluble being usually of a sweet taste, and the insoluble carbohydrates may be transformed into soluble by hydrolytic treatment. The monosaccharoses are colorless crystalline compounds, reducing alkaline solutions of the heavy metals as copper. Characteristic compounds are formed with phenylhydrazine.

The di- and poly-saccharoses are converted into simple carbohydrates when hydrolyzed, either by mineral acids or by enzymes.

The complicated carbohydrates of which cellulose is a type are amorphous, tend to form colloidal solutions, and relatively speaking, are chemically inert. By virtue of the hydroxyl groups which they contain, they react with nitric acid, organic acids and alkylating agents, forming esters and ethers, the detailed description of which forms the subject matter of the volumes in this series.

Classification of Celluloses. E. Fremy,[2] who has classified the celluloses and allied bodies, has distinguished them according to their chemical basis as follows:

(a) Celluloses proper, including normal cellulose, meta-cellulose and para-cellulose.
(b) Vasculose, identical with lignocellulose and found chiefly in woody fiber.
(c) Cutose, and
(d) Pectose, found in unripe, fleshy fruits and roots, and transformed under the influence of acids into pectins.

---

[1] R. Pribram, Ber. 1888, **21**, 2599; Wien. Akad. Ber. II b, **97**, 375; Monatsh. **9**, 395; abst. J. C. S. 1888, **54**, 1229; Bull. Soc. Chim. 1889, (3), **1**, 782; Chem. Ind. 1888, **11**, 554; Jahr. Chem. 1888, 2580; J. S. C. I. 1888, **7**, 594.

[2] Compt. rend. 1859, **48**, 667; abst. J. Pharm. (3), **35**, 321; Instit. 1859, 121; Rep. Chim. Pure, **1**, 351; Jahr. Chem. 1859, 534. Compt. rend. 1876, **83**, 1136; abst. Bull. Soc. Chim. 1877, **28**, 174; Ber. 1877, **10**, 90. His classification has not found favor with some critical writers.

There are a large number of substances, more or less, intimately related to cellulose, to which the term "compound-celluloses" has been applied. These compound celluloses are usually subdivided into the three following groups:

1. Pectocelluloses, which include most of the vegetable textile fibers with the exception of cotton, which forms a class by itself, and jute, which is a lignocellulose. The non-cellulose constituents are usually pectic substances, characterized as vegetable extractive bodies of an acid nature which readily gelatinize.[1] Unlike the adipocelluloses, they are said to be slightly richer in oxygen than normal cellulose, an analysis of raw flax (which is typical of this class) giving C. 43.7, H. 5.9, O. 50.4. On boiling with dilute alkali the pectocelluloses are readily resolved into cellulose, the pectic matters being transformed into soluble derivatives, and this is what takes place in the bleaching of linen. Many other fibers contain or consist of pectocelluloses,[2] these derivatives having been identified by E. Schunk in the products of the alkaline boiling of raw cotton.[3] The cellular portion of certain fruits (apple, pear, plum), and roots (turnip, carrot, beet) contain large amounts of pectocellulose.

Pectin, found in ripe fruit, is precipitable by alcohol and gelatinizes in boiling water, whereas pectose, found in unripe fruit, is substantially insoluble in water. Both are hydrolyzed by the action of alkalis and acids to intermediate compounds and finally to the hexoses and pentoses.

2. Lignocellulose comprises the main portion of all woody tissues as well as one textile fiber, jute, which in its raw state is richer in carbon than cellulose, and is readily attacked by acids, alkalis and oxidizing agents. Freely soluble in cuproammonium but incompletely precipitated upon acidifying, hence of but little value for the formation of artificial filaments in imitation of silk. Nitric and sulfuric acids, nitrate jute (see nitro-jute), the gain in weight being approximately the same as that of cotton

---

[1] A. Müller (Leipzig, 1904), abst. Zts. anorg. Chem. **39**, 121; Jahr. Chem. 1904, 100; Zts. ang. Chem. 1904, **17**, 970; has compiled a bibliography of colloids with 350 original publications cited; and Whitney and Ober (J. A. C. S. 1901, **23**, 856; abst. J. C. S. 1902, **82**, 65; Jahr. Chem. 1901, 133) have compiled an index to the literature of the same subject.

[2] C. Webster, J. C. S. 1883, **43**, 23; abst. Jahr. Chem. 1883, 1638; Chem. News, 1882, **46**, 240.

[3] Proc. Manchester Lit. Phil. Soc. (3), **4**, 95.

cellulose, and like the cellulose nitrates, give no amido products upon reduction, thus indicating true nitric esters. According to Sachsse lignocellulose consists of about 75 per cent. cellulose and the balance lignin, a body of an aldehydic character. Iodine is absorbed by jute, the resulting compound being about as unstable as starch iodide. This reaction has been taken advantage of in the quantitative determination of lignocelluloses in combination with other forms of cellulose. Dilute nitric acid acts upon jute at 80 degrees, forming oxycellulose, oxalic acid, carbon dioxide and a peculiar derivative of undetermined composition. The lignocelluloses hydrolyze much more readily than the simple celluloses, furfurol being obtained in considerable quantity when the temperature is raised to boiling. Glycolignose, the substance of fir and other Abies woods, and glycodrupose, the substance in the stony concretion of pears[1] are other forms of lignocellulose. "Crude fiber," a name applied to the residue obtained by boiling fodder plants with alkaline and acid solutions, has been found in most cases to consist of lignocellulose.

C. Cross and E. Bevan[2] have drawn attention to certain diversities in the cellulose group as a whole, especially as to the degree of resistance to hydrolytic and oxidizing agents; the amount of furfural yielded by decomposition with aqueous HCl; and the ratio between carbon and oxygen. The following table has been constructed by them as indicating these points of divergence:

Type	Cotton Group. Bleached Cotton	Wood Cellulose Group. Jute Cellulose	Cereal Cellulose Group. Straw Cellulose
Carbon content..	44.0–44.4	43.0–43.5	41.5–52.5
Oxygen content..	0.50	0.51	53
Furfural.........	0.1–0.4	30.–6	12.0–15
Other characteristics..........	No active CO groups	Some free CO groups	CO groups very reactive

The lignocelluloses are in general, therefore, compounds of the formula $ROCH_3$ in which "R" represents, probably, aromatic

---

[1] Ber. 1899, **32,** 2493; abst. J. S. C. I. 1899, **18,** 940; Chem. Centr. 1899, II, 752; Meyer Jahr. Chem. 1899, **9,** 300; J. C. S. 1899, **76,** i, 852; Jahr. Chem. 1899, 1290; Bull. Soc. Chim. 1900, **24,** 620.

[2] J. C. S. 1895, **67,** 433; abst. Jahr. Chem. 1895, 1349; Rev. gén. sci. 1895, **6,** 295; Ber. 1895, **28,** R, 645; Wag. Jahr. 1895, **41,** 1028.

groups. These celluloses are characterized by forming compounds with the halogens and are resolved by chlorination into cellulose and chlorinated derivatives of aromatic compounds which are soluble in alkalis and in dilute sulfite solution, the pure cellulose thus being liberated.

3. Adipocellulose forms the outer or epidermal layer of leaves and fibers, readily transformed by oxidation with nitric acid into products similar to those split off by the oxidation of fats, together with cellulose. They are of a cellular rather than of a fibrous character, richer in carbon and poorer in oxygen than cotton cellulose and comprise the main constituents of the leaves, fleshy fruits and stems of annuals. The chief adipocelluloses are cork and bark, which, when the impurities are removed, leave a neutral body called cutose. Such materials always contain also a large proportion of oils. The chemistry of these bodies as yet has been but imperfectly investigated.

The waxes contain lignocellulose and nitrogenous substances. The adipocelluloses and cutocelluloses contain a larger percentage of carbon than pure cellulose, whereas the pectocelluloses have a higher proportion of oxygen.

B. Tollens[1] states that both hydrocellulose and all crude oxycellulose preparations contain cellulose, and that from the action of alkalis upon these bodies the conclusion is drawn that the true products of reaction (e. g., celloxin) are combined with these celluloses somewhat after the manner of esters. Tollens divides the cellulose group into the following four classes:

(a) Celluloses.
(b) Hydrated celluloses, i. e., hydrocellulose and hemicelluloses, bodies which are non-reducing, but readily hydrolyzed to reducing compounds.
(c) Cellulose with acid, i. e., carboxyl groups; this class includes the pectins, etc.
(d) Celluloses with both acid (carboxyl) groups and aldehydic or ketonic groups; this class includes the oxycelluloses which are cupric reducing bodies.

The more highly oxidized classes (c) and (d) are distin-

---

[1] Ber. 1901, **34**, 1434; abst. J. S. C. I. 1901, **20**, 740; Bull. Soc. Chim. 1902, (3), **28**, 269; J. C. S. 1901, **80**, i, 453; Jahr. Chem. 1901, 897; Chem. Centr. 1901, II, 39.

guished from (a) and (b) by elementary analysis, the ratio of H: O being 1:8–9, instead of 1:8, as in the (a) and (b) classes.

G. Bumcke and R. Wolffenstein[1] have described a product of the action of hydrogen dioxide on cellulose which they termed "hydralcellulose." They assign a H:O ratio of 1:8 to this body, but it has been pointed out that their analyses might be equally within the limits of error for a body of the oxycellulose type with a ratio of 1:8.3. Judging from the undoubted oxycellulose properties of "hydralcellulose," Tollens regards it as belonging to class (d) and sees no reason for modifying the view that oxycelluloses are true oxidation products of cellulose.

The acid cellulose derivatives and pectins are gelatinous bodies containing an excess of oxygen corresponding to the presence of carboxyl groups, aldehydic or cupric reducing groups being absent. The natural members of this class often contain besides the C_6 cellulose aggregate, groups which yield pentoses on hydrolysis. The author also includes gum tragacanth in class (c). Although A. Hilger and W. Dreyfus[2] came to the conclusion that the acid properties of tragacanth and oxybassorin could not be due to carboxyl groups, the author taking into account the inconclusive nature of the elementary analyses in this respect, prefers to regard both bodies as containing excess of oxygen over the normal carbohydrate 1:8 ratio, owing to the presence of carboxyl groups.

R. Wolffenstein and G. Bumcke[3] have shown that in Tollen's classification of the cellulose group of carbohydrates, the hydrocelluloses are recorded as hydrated or hydrolyzed derivatives, while the oxycelluloses are merely oxidized products. They contend it is hardly probable that the natural hydrolyzing tendencies of the acid reagents employed should be inhibited by the presence of the oxidizing agents. Tollens suggests that the cellulose in these products may be present combined with the

---

1. Ber. 1899, **32**, 2493; abst. J. S. C. I. 1899, **18**, 940; Chem. Centr. 1899, II, 752; Meyer Jahr. Chem. 1899, **9**, 300; J. C. S. 1899, **76**, i, 852; Jahr. Chem. 1899, 1290; Bull. Soc. Chim. 1900, **24**, 620.

2. Ber. 1900, **33**, 1178; abst. J. S. C. I. 1900, **19**, 677; Chem. Centr. 1900, I, 1217; Jahr. Chem. 1900, 838; Chem. Ztg. Rep. 1900, **24**, 159; Bull. Soc. Chim. 1901, (3), **26**, 269; J. C. S. 1900, **78**, i, 379.

3. Ber. 1901, **34**, 2415; abst. J. S. C. I. 1901, **20**, 925; Chem. Centr. 1901, II, 529; Jahr. Chem. 1901, 888; J. C. S. 1901, **80**, i, 582; Bull. Soc. Chim. 1902, (3), **28**, 368.

oxidized portion in the form of an ester but as this view implies condensation rather than hydrolysis, and the molecule of the product must be at least twice as large as that of the original cellulose, attention is drawn to the fact that if this were so the oxycelluloses ought to be more resistant to hydrolyzing conditions than the celluloses, whereas the reverse is invariably the case. These authors would classify this group of carbohydrates as follows:

A. Cellulose
B. Hydrated cellulose (hydrocelluloses)
    (a) Reducing ("Hydralcellulose");
    (b) Reducing and with carboxylic groups;
    (c) With carboxylic groups but non-reducing (acid-cellulose);
    (d) Neither reducing nor with carboxylic groups (lactone configuration).

"Hydrocellulose" being produced by so mild a reagent as a 3 per cent. solution of hydrogen peroxide, is regarded as a purely hydrolytic product without the formation of any more highly oxidized groupings. Cellulose may be isolated from vegetable raw material by boiling the tissue in solutions of 1 to 5 per cent. sodium hydroxide and after washing, exposure of the moist mass to the vapors of chlorine or fluorine gas or to bromine water at the ordinary temperature. Alkaline hydrolysis, i. e., boiling in alkaline solutions as sodium sulfite, sodium carbonate or sodium hydrate, dissolves away the products formed from the non-cellulose constituents in the preceding treatment. In dealing with unusually refractory materials such as the hard woods, it may be necessary to repeat this cycle of processes several times. The material is finally completely extracted with alcohol and ether in a Soxhlet extractor to remove resinous and fatty products not completely saponified by the previous alkaline treatments.

From this it follows that the typical celluloses are not separable from plant tissue in the pure state but in admixture or in intimate chemical union with other compounds or groups of compounds, which groups are distinguished by greater reactivity in that they more readily yield to alkaline hydrolysis, such as the pectic bodies; or to oxidation, as the coloring matters or to the action of the halogens. In this latter classification is properly included the very important group of lignone celluloses which are distinguished, according to Cross and Bevan, by the presence of cutohexane groups in union with the cellulose, and therefore capable of directly combining with the halogens.

Constitution of Cellulose. The various modifications of cellulose have been extensively investigated and many constitutional formulas for the normal cellulose molecule have been suggested. The percentage composition of the purest form of cellulose obtainable is: Carbon 44.2–44.4 per cent., hydrogen 6.2–6.3 per cent., and oxygen 49.4–49.5 per cent. These figures lead to the general formula $(C_6H_{10}O_5)_n$. It is difficult to determine the molecular weight of cellulose, owing both to its non-crystalline nature, and to the fact that no cellulose derivative is known which has been volatilized without undergoing chemical change. Although many formulas have been put forward no particular one hitherto has received general acceptation.[1]

Being a colloid, cellulose—like starch—comprises an aggregate of reactive constituent groups whose equilibria is continually being modified by the reactive process. It has variously been regarded as a polycyclohexane or polyhexose derivative containing CH_2OH, CHCOH and CO in addition to OH groups. Their number, as yet, has not been definitely ascertained.

The properties and reactions of normal and modified cellulose have as yet thrown but little light on the inner mechanics of cellulose orientation, but the following observations have been recorded, from which certain generalizations with profit may be drawn.[2,3,4]

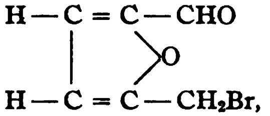
---

1. Cross and Bevan, "Cellulose," **3**, 10.
2. Cross and Bevan, "Cellulose," 75.
3. A. Green, J. Soc. Dyers Col. 1904, **20**, 117; Zts. Farb. Text. Chem. 1904, **3**, 97; abst. J. S. C. I. 1904, **23**, 382; Zts. ang. Chem. 1904, **17**, 1121; Chem. Centr. 1904, I, 1069; II, 980; J. C. S. 1904, **86**, i, 652; 1905, **88**, i, 22; Jahr. Chem. 1904, 1160, 1161; Chem. Ztg. Rep. 1904, **28**, 115; Wag. Jahr. 1904, **50**, II, 398.
4. E. Schulze, Ber. 1889, **22**, 1192; 1890, **23**, 2579; 1891, **24**, 2277; abst. J. C. S. 1889, **56**, 916; 1890, **58**, 1456; 1891, **60**, 238, 1178; 1892, **62**, 907; Bull. Soc. Chim. 1890, **4**, 522; 1891, **5**, 787; 1892, **8**, 491; Jahr. Chem. 1891, **44**, 2208; J. S. C. I. 1890, **9**, 1051; 1892, **11**, 49. W. Will, Ber. 1891, **24**, 400; abst. J. C. S. 1891, **60**, 542; Bull. Soc. Chim. 1891, **6**, 668; J. S. C. I. 1891, **10**, 578; Jahr. Chem. 1891, **44**, 1624. Chem. Centr. 1891, **62**, I, 530; Meyer Jahr. Chem. 1891, **1**, 333; Chem. Ztg. Rep. 1891, **15**, 90. H. Fenton and M. Gostling, J. C. S. 1898, **73**, 557; abst. Chem. Centr. 1898, **69**, II, 181, 421; Jahr. Chem. 1898, **51**, 1312; Meyer Jahr. Chem. 1898, **8**, 202; Chem. Ztg. 1898, **22**, 493.

(1) The action of hydrochloric acid releases carbonyl groups.

(2) Resolution by inorganic acids and subsequent hydrolysis into simple carbohydrate (dextrose) molecules.

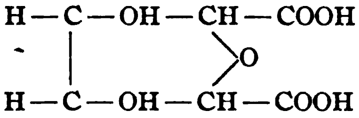
(3) Formation of the crystalline ω-bromomethylfurfural by the action of hydrobromic acid:



(4) Oxidation of cellulose to oxycellulose.

(5) Formation of furfural from oxycellulose by acid hydrolysis.

(6) Formation of isosaccharic acid from oxycellulose.



in addition to dioxybutyric acid by the action of a solution of calcium hydroxide.

(7) Resolution of cellulose by alkali fusion into oxalic acetic and hydroxypyruvic acids, carbon dioxide and hydrogen.

(8) Decomposition by bacterial action into methane, hydrogen, carbon dioxide and fatty acids (mainly acetic and butyric).

(9) Distillation in vacuo gives a good yield of *l*-glucosan.

(10) Stable nature of the cellulose molecule shown by its partial resistance to alkali hydrolysis, oxidizing agents and acetylation. When acted upon by concentrated alkaline solutions, such as caustic soda, an unstable sodium compound is formed. When this solution is diluted with water a cellulose is obtained which is more soluble in such solvents as

concentrated acid zinc chloride than the untreated cellulose.

(11) Synthetic reactions—formation of various nitrates, acetates and benzoates, and ethers.

(12) Formation of a trimethylglucose from methylated cellulose.

(13) Formation of oxypyruvic acid (CH_2 OH.CO.-COOH) by the action of dilute alkalis on nitrocellulose.

(14) The thiocarbonate reaction which gives indication of the nature of the hydroxyl groups and the resistance of the molecule to hydrolysis.

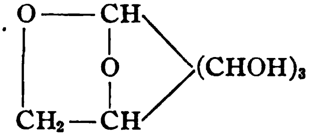
(15) Specific volume and solution volume determinations indicate that the cellulose molecule is, comparatively speaking, probably small.

The activity of certain groups in the cellulose molecule is suppressed. Thus, there are no free carbonyl groups present capable of reaction with phenylhydrazine or hydroxylamine. A study of the number of hydroxyl groups which react with acids to yield esters shows that there are probably only three such groups. (C_6). The highest nitrate of the unaltered cellulose complex is probably the trinitrate and the highest acetate probably the triacetate (C_6). It is possible to obtain analytical figures indicating a tetra-acetylcellulose, but this compound is most likely derived from a condensation product or other cellulose derivative. The three hydroxyl groups would require to be arranged in such a manner as to show their alcoholic function.

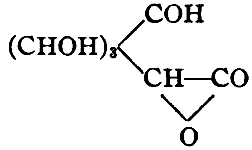
Again, any suggested formula for cellulose must show that one carbon atom is capable, on hydrolysis, of reacting as part of a carbonyl group. The results of the fusion with alkali indicate that the linking $CO.CH_2$ functions as an important unit in the grouping.

From the above considerations the choice lies between a cyclic and an open chain structure. As opinions differ in the interpretation of the known reactions and since no chemical synthesis of cellulose has been carried out, both types of formulas have their adherents. The formulas in some cases are proposed only tentatively. They are suggested in the main so as to offer a stimulus to future investigators and to act as a guide.[1,2]

L. Vignon,[3] from a study of the nitration of cellulose, oxycellulose and hydrocellulose, concludes that the cellulose molecule is a simple one. By the action of alkali on the nitration product of oxycellulose, W. Will obtained hydroxypyruvic acid.[4] His proposed constitutional formula is as follows:



The oxycellulose is considered to have the grouping:



---

1. E. Grandmougin, Chem. Ztg. 1908, **32**, 241; abst. J. C. S. 1908, **94**, i, 250; Chem. Zentr. 1908, **79**, I, 1617; Bull. Soc. Chim. 1909, **6**, 231. C. Schwalbe, Chem. Ztg. 1908, **32**, 287; abst. J. C. S. 1908, **94**, i, 321; C. A. 1908, **2**, 3142; Chem. Zentr. 1908, **79**, I, 1617. Compare A. Pictet, Arch. Sci. phys. et. nat. Geneva, 1915, (4), **40**, 181; abst. Chem. Zentr. 1916, **87**, I, 68; C. A. 1916, **10**, 1754.

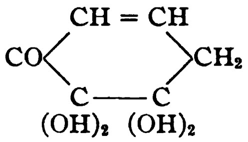
2. F. Beltzer, Rev. gén. chim. 1910, **13**, 72; abst. C. A. 1910, **4**, 1369; Chem. Zentr. 1910, **81**, I, 1596; Chem. Ztg. Rep. 1910, **34**, 135.

3. Compt. rend. 1898, **126**, 1355; abst. J. C. S. 1898, **74**, i, 620; J. S. C. I. 1898, **17**, 680; Chem. Centr. 1898, **69**, II, 24, 792; Jahr. Chem. 1898, **51**, 2265; Chem. Ztg. 1898, **22**, 425; Bull. Soc. Chim. 1898, **19**, 810; Mon. Sci. 1898, **51**, 454; Rev. gén. sci. 1898, **9**, 918. He obtained furfuraldehyde from various products as follows: hydrocellulose, 0.854%; oxycellulose, 2.113%; oxycellulose from chromic acid, 3.5%; reduced cellulose, 0.86%; starch, 0.8%; bleached cotton 1.8%. "Résumé of Investigations of Oxycellulose," Rey, Lyon, 1900.

4. W. Will, Ber. 1891, **24**, 400; abst. J. S. C. I. 1891, **10**, 578; J. C. S. 1891, **60**, 542; Chem. Centr. 1891, **62**, I, 530; Jahr. Chem. 1891, **44**, 1624; Chem. Ztg. Rep. 1891, **15**, 90; Bull. Soc. Chim. 1891, **6**, 668; Meyer Jahr. Chem. 1891, **1**, 333. Compare in this connection, A. Bechamp, Compt. rend. 1853, **37**, 134; abst. Jahr. Chem. 1853, **6**, 550. A. Hofmann, Ann. 1860, **115**, 283; abst. J. C. S. 1860, **13**, 76; Chem. Centr. 1860, **31**, 976; Rep. Chim. Appl. 1861, **3**, 119; Jahr. Chem. 1860, **13**, 499. S. De Luca, Compt. rend. 1861, **53**, 298; 1864, **59**, 487; abst. Jahr. Chem. 1861, **14**, 713; 1864, **17**, 570; Instit. 1861, 275; Dingl. Poly. 1861, **162**, 135; J. prakt. Chem. 1862, **85**, 378; J. Pharm. (3), **41**, 483; Poly. Centr. 1862, **28**, 221; Dingl. Poly. 1864, **174**, 388; Wag. Jahr. 1864, **10**, 243; Mon. Sci. 1864, **12**, 951; Poly. Centr. 1865, **31**, 197. Maurey, Compt. rend. 1849, **28**, 343; abst. Jahr. Chem. 1849, **2**, 471; Annuaire de Chim. 1850, 360. E. Divers, J. C. S. 1863, **16**, 91; Chem. News, 1863, **7**, 154; Zts. Chem. Pharm. 1863, 237; J. prakt. Chem. 1864, **91**, 58; Chem. Centr. 1863, **34**, 690; Bull. Soc. Chim. 1864, **1**, 46; abst. Jahr. Chem. 1863, **16**, 569. F. Kuhlmann, Compt. rend. 1856, **42**, 676; abst. Jahr. Chem. 1856, **9**, 821; Dingl. Poly. 1856, **142**, 221; Poly. Centr. 1856, **22**, 870; J. prakt. Chem. 1856, **69**, 288; Chem. Gaz. 1856, 192; Wag. Jahr. 1856, **2**, 327.

united with varying proportions of residual cellulose.

C. Cross and E. Bevan are of the opinion that a cyclic structure for cellulose best represents its relative stability compared with that of the hexoses. The formation of a cellulose tetra-acetate of the composition $C_6H_6O\ (Ac.)_4$ in which only 2 carbon valencies are taken up in outside" combination would point to a symmetrical formula. In the plant world the transition of cellulose to R-keto-R-hexene, and benzene derivatives, also support the formulation of cellulose as a cyclo-hexane derivative. The process of lignification in the plant cells is characterized by the formation of groups of the type of a cyclic tetra-hydroxyketohexene of the general formula:

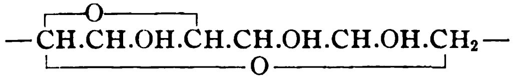


This form of grouping behaves in a similar manner to cellulose and it is considered probable that some such type of grouping would represent the simple cellulose molecule.

C. Cross and E. Bevan put forward the suggestion that cellulose may be a special form of a general carbohydrate of the formula:

$$n.[(CHOH)_3COC_2H_4O]$$

leaving the position of the carbonyl group and its type, i. e., whether aldehydic, ketonic or cycloketonic an open question. The special function of the oxygen atom is also not defined. The C_6 unit on the basis of 3(OH) groups for the normal cellulose has been represented by the formula:



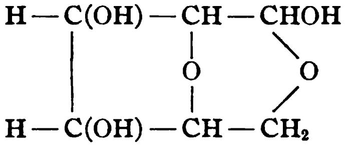
$$-\underbrace{\overbrace{\text{CH.CH.OH.CH}}^{\text{O}}\text{.CH.OH.CH.OH.CH}_2}_{\text{O}}-$$

A. Green[1] regards celluloses as having the constitution of an intermolecular anhydride of glucose, and to have the structural formula

---

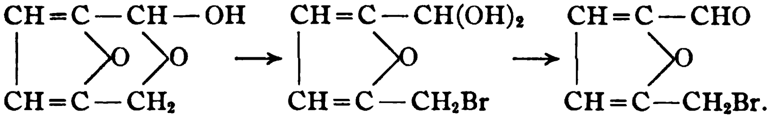
[1] A. Green, Zts. Farb. Text. Chem. 1904, **3,** 97; abst. J. S. C. I. 1904, **23,** 382; Chem. Centr. 1904, I, 1069; II, 980; Jahr. Chem. 1904, 1160, 1161; J. C. S. 1905, **88,** i, 22; Chem. News, 1906, **93,** 243; Soc. Dyers Col. 1904, **20,** 117; Zts. ang. Chem. 1904, **17,** 1121; abst. Wag. Jahr. 1904, II, 398; J. C. S. 1904, **86,** i, 652.

graphically represented by the following:



By such a formula most of the reactions of cellulose can be satisfactorily explained. It lends a ready explantion of the formation of dextrose by hydrolysis, and is also in agreement with the formation of a trinitrate and triacetate as the highest esters, for higher derivatives could only be obtained by the transformation of the two central oxygen atoms into two hydrooxyl groups.[1] The production of ω-bromo- and ω-chloromethylfurfuraldehyde in the cold, in good yield from normal cellulose, by the action of dry hydrogen bromide and chloride respectively, is explained on Green's formula, as well as why cellulose does not react with either phenylhydrazine or hydroxylamine, because it does not contain either aldehydic or ketonic carbonyls (CO) groups.

This is shown by the initial dehydration (I) and addition of the hydrogen halide (II), followed by further loss of the elements of water (III), thus:



I II III

The dehydrated product ($C_6H_6O_3$) has the empirical formula of lignone and is probably related to this latter substance.

He claims that an acceptable formula for cellulose must satisfactorily explain the following:

(1) A trinitrated derivative.

(2) A triacetated compound.

(3) Concentrated sodium hydroxide gives a compound, decomposable by water to form cellulose hydrate, and in this condition more soluble in zinc chloride and cuprammonium solutions than untreated cellulose.

(4) Treated with alkali and carbon bisulfide, cellulose

---

[1] C. Cross and E. Bevan, Zts. Farb. Text. Ind. 1904, **3**, 197, 441; abst. Chem. Centr. 1904, **75**, II, 197; 1905, **76**, I, 225; J. C. S. 1904, **86**, 1161; 1905, **88**, i, 119; Chem. Zts. 1904, **3**, 807; Jahr. Chem. 1904, **86**, 1161.

thiocarbonate forms, easily soluble in water.

(5) With phenylhydrazine or hydroxylamine, no reaction.

(6) When hydrolyzed with sulfuric acid, the ultimate product is glucose.

(7) Must respond to the Fenton reaction for chlormethylfurfural.

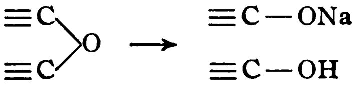
(8) Formation of oxycellulose by oxidation, which upon distillation with dilute sulfuric acid, gives furfural.

(9) The oxycellulose when boiled with milk of lime, gives dioxybutyric and isoglucosic acids.

(10) When nitrated, and the nitrocellulose treated with dilute NaOH, oxypyruvic acid is formed.

When normal cellulose is referred to, one generally associates it with the purest form of Swedish filter paper. This class of paper, however, receives very drastic treatment in purification and the cellulose is slightly attacked. It is claimed that cotton fiber, purified of its pectic bodies, fat and nitrogenous matter by the mildest possible treatment, gives the purest cellulose. Cotton as prepared in calico manufacture, is considered by C. Cross and E. Bevan to represent normal cellulose.

The behavior of cellulose on mercerization may be explained according to Green's formula by the "opening out" of the central oxide group:



$$\begin{matrix}\equiv C\\ \equiv C\end{matrix}\!\!>\!O \longrightarrow \begin{matrix}\equiv C-ONa\\ \equiv C-OH\end{matrix}$$

on washing with water a hydrated cellulose is formed $\left.\begin{matrix}-C-OH\\ -C-OH\end{matrix}\right\}$. In a similar manner the regeneration of cellulose from mononitrocellulose[1] may be explained.

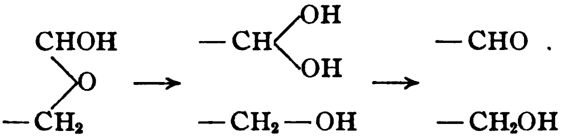
In the viscose reaction a similar "opening out" of the central oxygen occurs and on the elimination of the thiocarbonate group a hydrated cellulose again results.

The latent aldehydic character of cellulose is explained by

---

[1] E. Knecht, Ber. 1904, **37**, 549; abst. J. Soc. Dyers Col. 1904, **20**, 68; Rev. gén. chim. 1904, **4**, 413; J. S. C. I. 1904, **23**, 335; Chem. Centr. 1904, **75**, I, 872; J. C. S. 1904, **86**, i, 293; Bull. Soc. Chim. 1905, **34**, 514; Jahr. Chem. 1904, 1165; Chem. Ztg. Rep. 1904, **28**, 92.

assuming that the $—CH_2—O—\underset{|}{C}H—OH$ group is able to function as an aldehyde by the simultaneous taking up and removal of a molecule of water.



Against the formula of Green the objection has been raised that it does not account for the stability of cellulose towards alkali compared with the ease with which alkali attacks monoses. In addition, when viscose and alkali cellulose are hydrolyzed the reacting groups unite to form aggregates of higher molecular weight, a fact not made clear by Green's formula.

The doubt expressed by Green on the existance of a tetra-acetyl-cellulose obtained from a normal cellulose was finally settled by A. Green and A. Perkin.[1] They determined the amount of acetic acid obtainable from so-called tetraacetylcellulose by hydrolysis, both with sulfuric acid and with sodium hydroxide. The result of three series of determinations carried out under different conditions agreed with the theoretically possible values for a tri-acetylcellulose. This result is in conflict with the yield of ester obtained by other workers. It is in agreement, however, with the A. Green's formula and brings the highest normal acetate into line with the cellulose nitrates and benzoates. If "three" is regarded as the maximum number of reactive hydroxyl groups in the cellulose molecule, any cellulose esters containing more than three acid residues or their equivalent, should be considered as derived from hydrated celluloses. In this case the central oxygen group is converted into 2(OH). Into this category would be placed the aceticsulfuric ester $(C_6H_7O_2)_4SO_4(CH_3COO)_{10}$ obtained by C. Cross and E. Bevan, as well as certain other cellulose acetates.

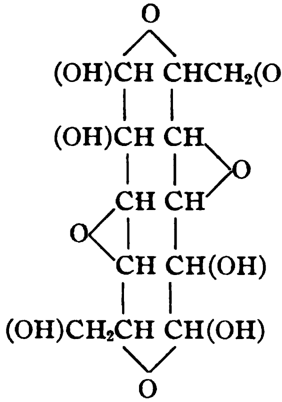
Green's formula is intended to represent cellulose in its

---

[1] J. C. S. 1906, **89**, 811; abst. J. Soc. Dyers Col. 1906, **22**, 230; Rev. gén. mat. color. **11**, 51; C. A. 1907, **1**, 1062; Bull. Soc. Chim. 1910, (4) **2**, 37; Jahr. Chem. 1905–1908, II, 985; Zts. ang. Chem. 1907, **20**, 459; J. S. C. I. 1906, **25**, 652; Chem. Ztg. 1906, **30**, 517; Rep. gén. chim. 1906, **6**, 331, 381; Chem. Centr. 1906, II, 321.

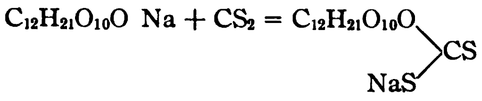
simplest or unpolymerized form. In such a form it may be supposed to exist in an ammoniacal cupric solution. The cellulose of fiber may be regarded either as a physical aggregate of these simple molecules, or less likley as a chemical polymer made up of a number of C_6 complexes united by their oxygen atoms.

H. Barthelemy[1] gives to cellulose the following constitutional formula:



The formation of oxycellulose of the general type n $(C_6H_{10}O_5)$-m $(C_6H_{10}O_6)$ is explained by assuming that one of the terminal —CH_2OH groups is oxidized to an aldehydic group. This view explains (a) the strong reducing power of oxycellulose; (b) it shows the hydrolyzing action of oxidizing reagents in the acetylation and formylation of cellulose, and (c) explains the formation of furfural in the distillation of cellulose in the presence of hydrochloric and sulfuric acids.

The formation of hydrocelluloses of the type n$(C_6H_{10}O_5)$-H_2O is explained by assuming that a molecule of water is attached to the $=HC—O—C=$ group in a manner similar to that postulated by A. Green. This viscose may be regarded as a product of the reaction

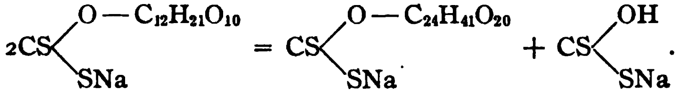


$$C_{12}H_{21}O_{10}O\,Na + CS_2 = \begin{matrix} C_{12}H_{21}O_{10}O \\ NaS \end{matrix}\Big\rangle CS$$

and the "ripening" as a polymerization

---

[1] Caout. & Guttap. 1917, **14**, 9274, 9328; abst. C. A. 1917, **11**, 3428; 1918, **12**, 223.



$$2CS\begin{matrix}O-C_{12}H_{21}O_{10}\\ SNa\end{matrix} = CS\begin{matrix}O-C_{24}H_{41}O_{20}\\ SNa\end{matrix} + CS\begin{matrix}OH\\ SNa\end{matrix}.$$

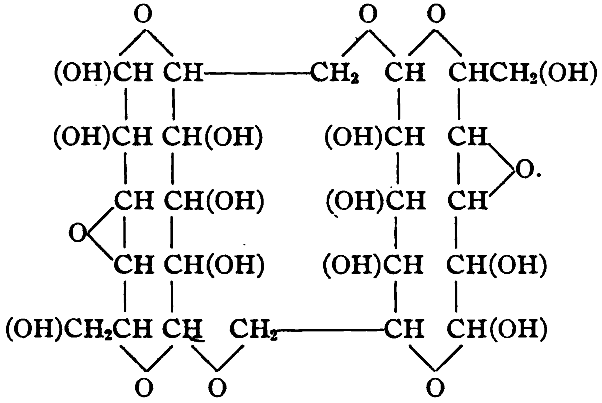
The general formula for cellulose xanthates being

$$CS\begin{matrix}O-C_{6m}H_{10m+1}O_{5m}\\ SNa\end{matrix}$$

and hydrocellulose

$$C_{6m}H_{10m+1}O_{5m}-OH, \text{ i. e., } m(C_6H_{10}O_5)_m.H_2O.$$

The condensation of the cellulose molecule is considered to take place laterally, an OH of the side chain splitting off with H from one of the groups functioning as a primary alcohol. The constitutional formula of the condensed product would be:



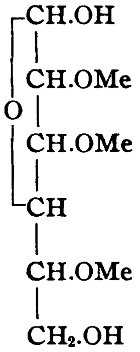
H. Barthelemy considers that the highest normal ester contains three acid residues (C_6). He was unable to obtain a formylcellulose containing more than three formyl groups (C_6). Similarly in trying to substitute other groups for NO_2 he notes that nitrocellulose dissolves in formic acid with denitrification.

From a study of the methylation of cellulose as undertaken by W. Denham and H. Woodhouse[1] further insight may be

---

[1] J. C. S. 1913, **103**, 1735; 1914, **105**, 2357; abst. C. A. 1914, **8**, 243; 1915, **9**, 203; Chem. Zentr. 1913, **84**, II, 1857; 1915, **86**, I, 81; J. S. C. I. 1913, **32**, 974; J. Soc. Dyers Col. 1913, **29**, 327; Bull. Soc. Chim. 1913, (4), **14**, 1495; see also L. Lilienfield, F. P. 447974, 1912; abst. J. S. C. I. 1913, **32**, 420, 940; E. P. 12854, 1912; Belg. P. 254591, 1912; abst. J. C. S. 1913, **103**, 1747; C. A. 1913, **7**, 3839; Mon. Sci. 1914, **80**, 3; Kunst. 1913, **3**, 195. See also E. P. 6035, 1913; abst. J. S. C. I. 1914, **33**, 417.

obtained with respect to the constitution of cellulose. These workers first allowed their fibrous material to be impregnated with a 15% solution of caustic soda, the material after removal from this solution being methylated by the direct action of methyl sulfate. Various alkyl substituted sugars were obtained. From the number and distribution of these alkyl groups it is suggested that a clue may be obtained regarding the union of the monosaccharide residues in the original cellulose material. From the methylated cellulose is obtained a crystalline trimethyl-glucose:



This result indicates the probable existence of at least three hydroxyl groups in the original cellulose aggregate.

Although the dry distillation of an organic compound is often so drastic a treatment as to fundamentally alter the constitution, yet a reference may be made to an experiment by A. Pictet and J. Sarasin.[1] In the dry distillation of cellulose they obtained *l*-glucosan in good yield (45%) and upon this the claim has been made that cellulose may be considered as a polymeride of *l*-glucosan. A constitution similar to that suggested by Green is proposed. The trimethylglucose obtained by W. Denham and H. Woodhouse from methylated cellulose by hydrolysis is not readily explained on the assumption that cellulose is a derivative of *l*-glucosan. Throughout the literature on cellulose, some confusion exists whether cellulose should be regarded as $C_6H_{10}O_5$, or some multiple of this, due to the fact that

[1] Compt. rend. 1918, **166**, 38; abst. J. C. S. 1918, **114**, i, 59; C. A. 1918, **12**, 804; Helvetica chim. acta. 1918, **1**, 78; abst. C. A. 1918, **12**, 2187; Arch. sci. phys. nat. 1918, **46**, 5; Chim. and Ind. 1918, **1**, 279; J. S. C. I. 1918, **37**, 49-A.

up to the present the molecular weight of cellulose is unknown. Determinations of the molecular weight of cellulose esters such as nitrates, acetates, and benzoates have given abnormal results, and have usually varied sufficiently to prevent useful comparisons being made. By determinations of the molecular weight of triacetylcellulose by the boiling point method in a Beckmann apparatus a value of approximately 40 for the molecular weight of cellulose is indirectly obtained.[1] This is approximately a quarter of the molecular weight required for the simplest formula $C_6H_{10}O_5$. Much of the difficulty in the way of determining the molecular weight is due to the colloidal and amorphous nature of both celulose and the majority of its derivatives.

W. Dreaper regards cellulose as an aggregate of ions which take their origin in the plant cells in which the celluloses are present as mass aggregates. From this standpoint cellulose is a typical colloid with no fixed constitutional formula, and is to be regarded rather as a unit in dynamic equilibrium, its reacting unit at any moment being a function of the condition under which it is placed.

A. Green advocates the use of the simple formula $C_6H_{10}O_5$ for cellulose rather than a multiple of this. He argues that although cellulose is a colloid, there is no reason why it should be regarded as having a high molecular weight, as inorganic colloids are known to which simple formulas are given. The formula $C_{12}H_{20}O_{10}$ for cellulose has also been advocated. The existance of tri- and penta-cellulose nitrates of the type $C_{12}H_{17}O_{10}(NO_2)_3$ and $C_{12}H_{15}O_{10}(NO_2)_5$ would require a molecule containing twelve carbon atoms. Other reactions furnish evidence as to the com-

---

[1] A. Nastjukow, J. Russ. Phys. Chem. Soc. **32,** 543; Ber. 1900, **33,** 2237; 1901, **34,** 719; abst. Chem. Centr. 1901, **72,** I, **99,** 932; J. C. S. 1900, **78,** i, 540; 1901, **80,** i, 315; Bull. Soc. Chim. 1901, **26,** 123, 557; Jahr. Chem. 1900, **53,** 844; 1901, **54,** 897, 898; J. S. C. I. 1900, **19,** 733; 1901, **20,** 573; 1902; **21,** 63. O. Faber and B. Tollens, Ber. 1899, **32,** 2589; abst. Chem. Centr. 1899, **70,** II, 901; J. S. C. I, 1899, **18,** 1014; J. C. S. 1899, **76,** i, 854; Jahr. Chem. 1899, **52,** 1292; Chem. Ztg. Rep. 1899, **23,** 321; Chem. Tech. Rep. 1899, **38,** 550; Bull. Soc. Chim. 1900, **24,** 621; compare also V. Zanotti, Annaurio Soc. Chim., Milano, 1899, 27; abst. Jahr. Chem. 1899, **52,** 1288; J. C. S. 1899, **76,** i, 851; Chem. Centr. 1899, **70,** I, 1209. G. Bumcke and R. Wolffenstein, Ber. 1899, **32,** 2493; abst. Chem. Centr. 1899, **70,** II, 752. Meyer Jahr. Chem. 1899, **9,** 300; J. C. S. 1899, **76,** i, 852; Jahr. Chem. 1899, **52,** 1290; Bull. Soc. Chim. 1900, **24,** 620; J. S. C. I. 1899, **18,** 940. A. Sabanejew, Jour. Russ. Phys. Chem. Soc. 1891, **23,** I, 80; abst. Zts. Physik. Chem. 1892, **9,** 89; Ber. 1891, **24,** R, 666; Bull. Soc. Chim. 1891, **6,** 719; Jahr. Chem. 1891, **44,** 122.

plexity of the cellulose molecule, as an aggregate.

Thus the production of cellobiose by Z. Skraup,[1] from cellulose, involves the assumption that the substance $C_{12}H_{22}O_{11}$ is either a degradation product of cellulose, or that it has been synthesized during the reaction. However, it may be unsafe to attach too much reliance on the evidence of reactions and combinations as the equilibrium of the molecule is prone to be modified by the process of reaction, the cellulose complex being regarded as a labile aggregate. Hydration or even condensation may also occur coincidental with, or previous to, chemical combination. As yet no accurate picture of the cellulose molecule can be presented, and suggested equations of reactions involving the cellulose complex can only be approximate representations of what takes place.

Preparation of Pure Cellulose. In order to obtain pure cellulose for industrial purposes or for scientific investigation, it is necessary to remove the extraneous impurities, coloring matter and incrusting materials.

This may be conveniently carried out according to the following suggested method of treatments. The cotton (or other form of cellulose) is first mechanically treated for the removal of foreign impurities, and then boiled preferably under 3 to 5 atmospheres pressure with a 1%-2% solution of sodium hydroxide, either with or without the presence of saponified oils. After thorough washing until the wash waters are colorless or substantially so, the cellulose is exposed in the moist state to the action to dilute chlorine, washed, treated with a dilute mineral acid in the cold, washed again to neutrality, and once again submitted to hot alkali treatment with subsequent removal of the alkali by washing. After drying, the cellulose may be extracted with hydrofluoric acid to remove fractions of a per cent. of iron and silica, and the cellulose finally exhausted with ether or petroleum benzine to remove the last trace of cholestrin and fatty materials. If the above indicated processes of purifica-

---

[1] Ber. 1899, **32**, 2413; abst. J. C. S. 1899, **76**, 852; Jahr. Chem. 1899, **52**, 1288; J. S. C. I. 1899, **18**, 941; Chem. Centr. 1899, **70**, II, 752; Bull. Soc. Chim. 1900, (3), **24**, 619. Z. Skraup and J. Koenig, Ber. 1901, **34**, 1115; J. S. C. I. 1901, **20**, 740; J. C. S. 1901, **80**, i, 370; Jahr. Chem. 1901, **54**, 878; Chem. Centr. 1901, **72**, I, 1197; Monatsh. 1901, **22**, 1011; abst. Chem. Centr. 1902, **73**, I, 183; J. S. C. I. 1902, **21**, 144.

tion have been carefully carried out, but little change in the structure of the cellulose will result.

F. Beltzer has described the following process for the preparation of normal pure cellulose from cotton: The cotton is first carefully combed in order to remove all mechanical impurities, than boiled for 6–8 hours in a solution of caustic soda of 1.013 sp. gr. The liquor is then squeezed out and the material washed until the waters are colorless or nearly so. The cotton is then treated with HCl of 1.01 sp. gr. at 45°–50° for 3–4 hours, and thoroughly washed. The fiber is next carefully bleached in a solution of sodium hypochlorite of 1.01 sp. gr. at 30° for 6–8 hours and washed in warm water. A second treatment as above is given the cotton. The cellulose is finally treated with a solution of sodium bisulfite of 1.01 sp. gr. at 55° for 5 hours, then well washed. When dried at a moderately low temperature, the cotton should give on ignition not over 0.05% ash. Cellulose thus prepared should be substantially insoluble in weak caustic soda or potash upon boiling, thus indicating the absence of hydrocellulose or oxycellulose. Should these impurities be present, they may be removed by again boiling the cellulose with caustic soda solution as before, followed by acidulation with hydrofluoric acid, treated with bisulfite, and washing. Cellulose thus prepared should give no furfural upon distillation with hydrochloric acid, nor show a rose color with phloroglucinolhydrochloric acid. The copper value with Fehling's solution should be nearly, if not quite, zero.

E. Rinman[1] purifies cellulose substances by boiling in a solution of calcium hydroxide in the presence of substances which increase the solubility of the calcium hydroxide. The method of the Zellstoffabrik Waldhof[2] is similar. W. Whitney[3] has described

[1] Can. P. 180925, 1917; abst. C. A. 1918, **12**, 1125; U. S. P. 1202317, 1916; abst. Mon. Sci. 1917, **85**, 50; J. S. C. I. 1916, **35**, 1215; C. A. 1917, **11**, 99. D. R. P. 285752, 1914; abst. J. S. C. I. 1915, **34**, 1139. Norw. P. 20645, 1909; abst. Mon. Sci. 1915, **83**, 56. C. Flodquist, U. S. P. 525540, 1894.

[2] Swiss P. 3194, 1891. E. P. 336, 1891; abst. J. S. C. I. 1892, **11**, 180. D. R. P. 64878, 1890; abst. Ber. 1893, **26**, R, 78; Wag. Jahr. 1892, **38**, 371; Ztg. ang. Chem. 1892, **5**, 706.

[3] U. S. P. 923227, 923745, 1909; abst. J. S. C. I. 1909, **28**, 743; C. A. 1909, **3**, 2091. C. Kellner (Belg. P. 166688, 1902; 170871, 171192, 1903) bleaches the fiber by the electrolysis of soluble chlorides. E. Nemethy (Belg. P. 196647, 1906) prefers magnesium mono- or bi-sulfite. See Elektro-Osmose Akt.-Ges. (Graf Schwerin-Ges.) D. R. P. 296053, 1917; Chem. Zentr. 1917,

a process for the purification of porous cellulose materials, wherein the porous material is washed with a solvent which is isotonic with respect to the impurity it is desired to remove and only contains a small quantity of it, while at the same time an electric current may be passed through the solvent. The process is more particularly applied to the removal of zinc chloride from cellulose, by suspending the cellulose in a liquid which will dissolve the impurity and passing an electric current through the solution.

P. Girard[1] proposed to purify the cellulose by a final treatment with methyl alcohol and formaldehyde. The I. Kitsee[2] process for cellulose purification preliminary to the employment of the cellulose for nitration purposes, and its utilization for battery cell jars and insulation plates, embraces first treating the cellulose with sodium carbonate solution as long as extractive forms, when it is washed until neutral, carefully dried and is then considered suitable for purposes of nitration.

In the purification of cellulose, especially for the manufacture of spinning solutions, the Verein f. Chemische Industrie in Mayence[3] have found that while readily soluble varieties of cellulose yield compounds which spin easily, the artificial silk threads thus produced are inferior in respect to tensile strength. On the other hand the observation has been made, that the most difficultly soluble varieties of cellulose yield filaments of the maximum tensile strength.

Their process has in view the treatment of the cellulose to render it sufficiently soluble without impairing the strength of the filaments therefrom, and this is accomplished by treating the spinning solutions with such small amounts of acid or acid

---

88, I, 354; Chem. Ztg. Repert. 1917, **41,** 104; J. S. C. I. 1917, **36,** 593; D. R. P. 249983; 265628, 1911; abst. C. A. 1914, **8,** 303; D. R. P. 295043, 1915; Addn. to D. R. P. 265628, 1911; abst. C. A. 1918, **12,** 791; E. P. 2379, 27930, 1911. F. P. 16642, Addn. to F. P. 448230.

[1] Belg. P. 247992, 1912; abst. Kunst. 1913, **3,** 178. F. P. 443897, 1912; abst. J. S. C. I. 1912, **31,** 1120; Kunst. 1913, **3,** 15. See also D. R. P. 266140, 1912; abst. C. A. 1914, **8,** 827; Chem. Ztg. Repert. 1913, **37,** 684. See C. Piest, Papierfabr. 1914, **12,** 860; abst. C. A. 1914, **8,** 3362; J. S. C. I. 1914, **33,** 856.

[2] U. S. P. 900744, 1908; abst. J. S. C. I. 1908, **27,** 1220; C. A. 1909, **3,** 515.

[3] D. R. P. 290131, 1913; abst. C. A. 1916, **10,** 2803; Kunst. 1916, **6,** 109; Chem. Ztg. Repert. 1916, **40,** 96; Zts. ang. Chem. 1916, **29,** 144; Chem. Zentr., 1916, **87,** I, 352; J. S. C. I. 1916, **35,** 533. The J. Daniel and F. Benoist process for the manufacture of pure cellulose is described in Belg. P. 260276, 1913.

salts that the formation of oxycellulose or hydrocellulose is prevented. The cotton which is to be worked up into artificial silk is carefully bleached for the prevention of the formation of oxycellulose or hydrocellulose, then rinsed and acidified with dilute sulfuric acid. The mass is then rinsed with very soft water (condensation or distilled water if possible) until the wash liquor after the concentration of a large quantity no longer shows an acid reaction.

The cotton fiber itself then shows a strongly acid reaction. It need only be carefully treated to be ready for the preparation of spinning solutions. The cotton is allowed to stand for several days in a dry place before subjecting it to the solution process. If sufficiently soft water is not available the de-acidified cotton must be rinsed with water at 10°–12° hardness, then immersed in a final bath which contains 0.01–0.10% acid calculated on the weight of the material.

E. Berl[1] has called attention to the fact that in the treatment of cellulose by technical processes, in order to dissolve or esterify the cellulose, certain methods of treatment are customary which, according to the opinion of this author, signify an increase of reaction of the cellulose by the decrease of the molecular size. According to Berl relative differences in the molecular size of cotton can be established by measurement of the internal friction of solutions of the same percentage of esters prepared in an identical manner.

If for the manufacture of cuproammonia silk, the cellulose is subjected beforehand to mercerization the greater reactivity is considered due to the size of the molecule. If mercerized or unmercerized cottons are nitrated in an identical manner, the acetone solution of the cellulose nitrates show entirely different viscosities, so that the time of efflux of nitrate solution of the

---

[1] Zts. Schiess. Sprengst. 1909, **4,** 81; abst. J. S. C. I. 1909, **28,** 380; C. A. 1909, **3,** 1926; Chem. Zentr. 1909, **80,** I, 1275; Jahr. Chem. 1909, **62,** 384; Chem. Tech. Rep. (Jacob.) 1909, **33,** 194; Wag. Jahr. 1909, **55,** I, 431; D. R. P. 199885, 1907; abst. Chem. Zentr. 1908, **79,** II, 466; Chem. Ztg. Repert. 1908, **32,** 382; Zts. ang. Chem. 1908, **21,** 2233; Mon. Sci. 1911, **74,** 93; Chem. Tech. Rep. (Jacob.) 1908, **32,** 382; Chem. Ind. 1908; **31,** 454; J. S. C. I. 1908, **27,** 937; Wag. Jahr. 1908, **54,** II, 355; C. A. 1908, **2,** 3154; Meyer Jahr. Chem. 1908, **18,** 309. Berl reduces the size of the cellulose molecule by heating to 100 degrees in the presence of an indifferent inert gas, as nitrogen, and claims it as especially advantageous for the preliminary treatment of cellulose intended for subsequent nitration.

mercerized cotton is very much shorter than that of the cellulose nitrate prepared from ordinary cotton. Similarly the bleaching recommended in the preparation process, if oxycellulose is produced thereby, also shows a decrease in molecular size.

G. and A. Schaefer[1] prepare cellulose for artificial silk and esterification purposes by boiling the cellulose under pressure, and at a correspondingly high temperature, in a weak solution of sodium carbonate, a caustic alkali, and "tar benzin." It is then washed, treated with dilute sulfuric acid, the excess of water is removed, and is finally bleached with hydrogen peroxide.

Cellulose as a Colloid. The Technology of the Cellulose Esters is an enumeration of the commercial applications of typical colloid bodies. Cellulose, as well as its nitrates, acetates, xanthates and ethers, in all their soluble and thermoplastic modifications, constitute a group of exceedingly important industries, which may, in the true sense of the word be called colloid. Pure cellulose is a typical gel possessed of a beautiful ultramicroscopic structure, showing well-developed swelling phenomena and on solution yielding the highly viscous solutions which are characteristic of the hydrated emulsoids. From these solutions it may be precipitated by means of neutral salts or in presence of dehydrating agents such as ethyl alcohol.

Cellulose resists dissolution in all neutral liquid solvents, and those solutions, like zinc chloride, cuprammonium and the concentrated inorganic acids, are all of a colloidal nature. There is no question but what the cellulose complex is altered in constitution during the solution process, more or less hydrated cellulosic bodies being regenerated. The method of dissolving cellulose in various fluids and the characteristics of the solution thus formed, constitute a separate topic in this chapter.

If hydration is a condition of intramolecular distension whereby the surface reactions are largely increased and the absorption phenomena correspondingly developed,[2] the phenomena is reversible. F. Clyster[3] expresses it as "a progressive gelatinization of fiber walls, or the formation of a coating of colloidal cellulose on the surface of the fibers with a consequent loss of capillary power,"

[1] U. S. P. 879416, 1908; abst. J. S. C. I. 1908, **27**, 278.

[2] Ann. Rep. Soc. Chem. Ind. 1917, **2**, 128.

[3] Paper, 1915, **16**, 13; abst. C. A. 1915, **9**, 3129.

but in general, the action instead of being superficial is usually deep-seated.

The more general investigation of the preparation of colloidal solutions from cellulose has been undertaken by P. v. Weimarn,[1] who has studied in detail the conversion of cellulose into a gelatinous plastic material, and the physical characteristics of colloidal cellulose solutions. He has found that treatment of various forms of cellulose with aqueous salt solutions under definite conditions of concentration, pressure, temperature and duration of action, can bring about a multitude of changes in the physical conditions of the cellulose, often analytically indistinguishable, but susceptible of differentiation on physical grounds. The greater the solubility of the salt, the greater the ease with which it forms hydrates, and the more readily soluble (peptisable) is the cellulose in the solution. From these solutions various hydrated modifications are recoverable by the use of selective coagulants and precipitants, these cellulose gels being best known as constituting the artificial silk industries of the viscose, cuprammonium and nitrocellulose processes. The final products all show the characteristics of a hydrated emulsoid. The ageing of viscose preliminary to yielding a solution optimal for spinning; the ripening of cuprammonium solutions; the clarification of nitrocellulose lacquers and bronzing liquids, and the velocity of the internal changes in state of combination of cellulose esters with solid and semi-fluid plastifiers and high boilers, together with that scientifically little studied solid solution of nitrocellulose and camphor constituting celluloid, all represent industries comprising an unbroken change of colloid-chemical processes. The formation of vulcanized fiber; the preparation of parchment from the action of zinc chloride or sulfuric acid upon cellulose; the manufacture of cellulose acetate gels in benzol-alcohol mixture are additional examples of the intricate and almost complete permeation of colloidal phenomena constituting the industries of the technical application of cellulose and its esters.

The colloidal structure of cellulose was conjectured in a rather hazy and nebulous manner by Hellot[2] away back in 1800,

---

[1] Zts. Chem. Ind. Koll. 1912, **11**, 41; abst. J. S. C. I. 1912, **13**, 768; C. A. 1912, **6**, 3516; J. C. S. 1912, **102**, i, 679; Chem. Zentr. 1912, **83**, II, 817.

[2] See Schwalbe, "Neue Farbentheoren," Stuttgart, 1907.

in describing the spongy, net-like, honey-combed structure of "the pores of the wool." E. Mills and J. Takamine in 1883 speak of the absorption of acids and bases from solutions by means of "organic fibrous colloids".[1] A. Muller-Jacobs[2] two years later looked to the colloidal contents of the cells and the diffusion or osmosis through the membranes of the cell walls of plants as an explanation of the plausibility of his theory of dyeing.

M. Dekhuyzen[3] dilates on the "spongy" structures of the fibers in his researches published in 1886. In 1894, G. Schmidt[4] accepting as a fact that the absorption of gases by porous substances such as charcoal has been shown to obey Henry's law, made experiments with dilute solutions including picric acid with cellulose—the concentration being calculated for the undissociated acid—but found that in no case was the law of Henry obeyed.

O. Witt[5] regarded all fibers without exception to consist of substances strictly to be classed as colloids, and hence all endowed with osmotic properties, i. e., they permit, owing to their molecular constitution, unobstructed passage for the dialysis and osmosis of the class of crystalloids. This idea was corroborated

[1] Jour. Chem. Soc. 1883, **43**, 153; abst. Jahr. Chem. 1883, **36**, 1784; Ber. 1883, **16**, R, 973; C. N. 1882, **46**, 299.

[2] J. Soc. Dyers Col. 1885, **2**, 95.

[3] Centr. Med. Wiss. 1886, 931, 945; abst. Ber. 1887, **20**, 518. W. Lewis, J. S. C. I. 1919, **38**, 1–T. W. Bancroft, Jour. Frank. Inst. 1918, **185**, 29, 199, 373; abst. C. A. 1918, **12**, 111, 552, 783; J. S. C. I. 1918, **37**, 173-A; J. C. S. 1918, **114**, ii, 13; Chimie et Ind. 1918, **1**, 278; J. Phys. Chem. 1918, **22**, 22.

[4] Zts. physikal. Chem. 1894, **15**, 56; abst. J. Chem. Soc. 1895, **68**, ii, 39; Chem. Centr. 1894, **65**, II, 830; Jahr. Chem. 1894, **47**, 98; Meyer Jahr. Chem. 1894, **4**, 32, 576; Ber. 1894, **27**, 845-R. See also Monatsh. Chem. **14**, 8; abst. Zts. anorg. Chem. 1894, **5**, 96. W. Harkins, E. Davies and G. Clark, J. A. C. S. 1917, **39**, 354, 541; abst. C. A. 1917, **11**, 731, 1588; J. C. S. 1917, **112**, ii, 238, 239. See also I. Langmuir, Phys. Rev. 1915, **6**, 79; abst. C. A. 1916, **10**, 992. R. Tolman and A. Stearn, J. A. C. S. 1918, **40**, 264; abst. C. A. 1918, **12**, 589; J. S. C. I. 1918, **37**, 131-A. See also R. Tolman, J. A. C. S. 1913, **35**, 307, 317; Science, 1916, **44**, 565; C. A. 1917, **11**, 4. Patrick, Science, 1916, **43**, 747.

[5] Faerb. Ztg. 1890–1891, Pt. 1; Zts. Phys. Chem. 1891, **7**, 93; abst. J. S. C. I. 1891, **10**, 42; Zts. ang. Chem. 1891, **4**, 62; Chem. Centr. 1890, **61**, II, 1039; Jahr. Chem. 1892, **45**, 2918; Meyer Jahr. Chem. 1891, **1**, 20; Chem. Ztg. 1890, **14**, 310; Wag. Jahr. 1890, **36**, 1121; Bull. Soc. Chim. 1891, **6**, 613; Mon. Sci. 1891, **37**, 694. H. Proctor and J. Wilson, J. C. S. 1916, **109**, 307; abst. C. A. 1916, **11**, 1051; J. S. C. I. 1916, **35**, 645; J. Amer. Leather Assoc. 1917, **12**, 76. See also J. C. S. 1914, **105**, 313, 326; J. S. C. I. 1916, **35**, 156, 404, 675; J. Amer. Leather Assoc. 1916, **11**, 399; abst. C. A. 1915, **9**, 875; 1916, **10**, 1807, 2052.

and carried a step further in 1900 by P. Zacharias[1] who established in considerable detail the colloidal nature of the textile fibers, and especially that of cotton cellulose. He emphasized the fact that will be repeatedly exemplified in the succeeding pages of this series of volumes, that the high molecular weight and proneness to reactivity of cellulose and the esters and ethers derived therefrom, and the fact that none of these compounds have been crystallized, distilled unchanged, or otherwise lent themselves to the usual methods of purification preparatory to analysis, have materially deterred investigators from penetrating into the inner histological anatomy of cellulose and its esters.

It is peculiar that in the various detailed bibliographies of colloids which have been published from time to time, cellulose is conspicuous by its absence among the materials investigated and reported upon, and this shows how virgin is, the entire field even at the present day. Colloid chemistry up to the present has concerned itself principally with inorganic substances, gelatin and agar-agar, and to a lesser degree with starch. The interrelations of nitrocellulose stability and colloid chemistry, and the practically untouched field of uni- and poly-solvent cellulose ester combinations offer an oasis for investigation of practically limitless potentialities.

C. Cross holds to the view that, regarding cellulose from the viewpoint of the ionic theory, it must be considered as a molecular aggregate consisting of a mixture of ions of heterogeneous dimensions. Hence, as a typical colloid, cellulose has no definite reactive unit as a body which takes the crystalline form, nor a fixed molecular constitution which may be represented within the limits of a constitutional formula; for the cellulose molecule cannot be regarded as a static unit, but rather as a dynamic equilibrium; its reacting unit at any one time being a function of

[1] Faerb. Ztg. 1901, **12,** 149, 158, 161, 167; abst. J. S. C. I. 1901, **20,** 804; J. C. S. 1902, **82,** i, 635, 725; Chem. Centr. 1901, **72,** II, 379, 513; Jahr. Chem. 1901, **54,** 1408; Meyer Jahr. Chem. 1901, **11,** 450; Chem. Ztg. 1902, **26,** 289, 680; Repert. Chimie, 1901, **1,** 111; Meyer Jahr. Chem. 1901, **11,** 450; Rev. Mat. Col. 1900, **4,** 307; Rev. gén. sci. 1902, **13,** 166; Rev. Phys. et Chimie, 1901, 41; Zts. Phys. Chem. 1902, **39,** 468; abst. Bull. Soc. Chim. 1902, **28,** 678. See also C. Weber, J. S. C. I. 1894, **13,** 120. Krafft, Ber. 1899, **32,** 1608; abst. J. S. C. I. 1899, **18,** 757. A. Sunderland, Paper. 1917, **20,** No. 4, p. 13; abst. C. A. 1917, **12,** 1544; J. S. C. I. 1917, **36,** 592. R. Hatch, Paper, 1917, **21,** No. 4, p. 41. C. Moe, Paper, 1911, **15,** No. 26, p. 18.

the conditions surrounding it. This view has been disputed.

W. Bovard[1] defines cellulose as a sponge-like structure of colloidal particles held together by capillary attraction. To this aggregate he attributes the power of absorbing hydroxyl ions, which would naturally be more abundant in an alkaline solution, and thus explains the more rapid hydration of cellulose in the presence of alkalis.

It should be remembered that the gel-forming properties of cellulose are produced as the result of chemical treatment which entirely destroys the morphological structure of the fiber, i. e., the fibrous structure is obliterated in passing into the colloid phase. This has recently been elaborated by J. de Cew,[2] and W. Gesell and J. Minor,[3] in investigating the conditions under which pulp hydrates upon prolonged beating.

In Volume Eight of this series, published in 1915, are to be found many examples in connection with the various normal and partially hydrated cellulose acetates and formates of gelatinization in alcohol or alcohol-benzol solutions, which are soluble and fluid when warm, but gelatinize as the solution cools, and finally solidify to a paste which may be again liquified by the application of heat.

According to J. Minor,[4] "cellulose may be considered as a sponge-like structure of colloidal particles, held together by certain unused, residual affinities, and these particles are only brought into solution by some salt like zinc chloride which, through the formation of a double salt, is capable of breaking apart the sponge-like structure. As a colloid with a very large amount of surface exhibiting positive residual affinity, cellulose is capable of adsorbing from the water solvent sufficient hydroxyl ions to give to the molecule as a whole a very strong negative charge. These highly charged particles are capable of swelling, or absorbing water, as dried

---

[1] Paper, 1918, **22**, 11; abst. C. A. 1918, **11**, 1251. S. Webb, U. S. P. 1201402, 1916; abst. J. S. C. I. 1916, **35**, 1215. V. Fishburn and O. Weber, Paper, 1916, **19**, No. 5, p. 13; abst. C. A. 1917, **11**, 887.

[2] Paper, 1916, **20**, No. 11, p. 13; Paper Makers Monthly, **55**, 175. See also J. S. C. I. 1917, **36**, 357; abst. C. A. 1917, **11**, 1901. Paper Makers Monthly, 1916, **54**, 334; abst. C. A. 1917, **11**, 209. O. Kress and G. McNaughton, Paper, 1917, **20**, No. 17, p. 13, 443, 527; abst. C. A. 1917, **11**, 2542.

[3] Paper, 1919, **24**, 527; abst. C. A. 1919, **13**, 1925. See W. Bovard, Paper, 1918, **22**, 43.

[4] Private communication.

jelly does. The hydration of cellulose may be defined as the absorption of hydroxyl ions by the surface of the colloid, followed by the slower absorption of water."

"Also, the close proximity of these adsorbed hydroxyl ions on the surface of the colloid is quite sufficient to bring about the formation of hydrocellulose by hydrolysis. This process is apparently the one utilized by plant life for the conversion of the cellulose of the cell wall into mucilage, as well as the explanation of the formation of artificial parchment by the long beating of wood pulp. This hydrolyzed cellulose is very much more susceptible to oxidizing agents than is cellulose and its formation is probably an intermediate step in the formation of oxycellulose."

The gelatinization of non-esterified cellulose has engaged the attention of J. Briggs,[1] who has investigated the pulp slime produced in a paper makers hollander. He perceives it as a hydrogel influenced by both chemical and mechanical means, and in which the hydration which enters only with water—and not with alcohol or benzene—is reversible in certain grades. Mechanical attrition favors gel formation. Concomitant with hydration goes increased absorptive powers and greater hygroscopicity. Briggs has conceived this as a special case of absorption between the solid and gaseous phases. Coincidental with hydration appears a lessening of the internal friction by the formation of viscous solutions of hydrated celluloses.

Cellulose fibers swelled with water, appear to again give up this moisture in an atmosphere of steam, a property also noted with gelatin. The removal of moisture from wood by superheated steam, and the coagulation of artificial cellulosic filaments by steam are corresponding illustrations.

The characteristic coagulation phenomena of colloids may be observed in many cases in cellulose solutions. In the formation of the cellulose of Guignet the material is said to be separable in flakes by precipitation with brine. Cuprammonium, zinc chloride and viscose solutions of cellulose are obtained in the solid form by precipitating or coagulating operations. Certain celluloid substitutes, as the phenol-aldehyde condensations are interesting from a colloid-chemical viewpoint in that they are

[1] Papierfabr. 1910, **8**, 46; abst. J. S. C. I. 1910, **29**, 874.

typical isocolloids, i. e., dispersoids in which the dispersed phase and the dispersion medium are polymers of each other.

As to the question as to which class of colloids cellulose is to be grouped, Muller[1] considers them to be a colloid gel, capable of swelling and possessing cell-like structure as indicated by the phenomena of swelling, gelatinization and absorption and therefore most appropriately falling into the "emulsoids." If Cross and Bevan are correct in that cellulose does not act as a polymer formation from degraded or depolymerized hexose groups of known structure, but as labile complex of groups with varying dimensions which are in a condition analogous to a salt solution of an electrolyte, then it appears that the cellulose is more reactive as a solvent aggregate than by succeeding molecular combinations. In the succeeding topics of the properties of the celluloses, are indicated some of the physical explanations of the foregoing statements and conceptions.

Reactivity of Cellulose. The observation of A. Muller[2] that filter paper possesses the property of precipitating from baryta water quite considerable quantities of baryta, finds corroboration in the work of H. Weiske.[3] Cold, dilute acids, either mineral or organic, have an almost inappreciable action upon purified cellulose, at most but a slight adsorption of compounds taking place. With acids of higher concentration (up to 40%) hydrocellulose formation results,[4] whereas with acids of 6%–8% strength, the tendency toward the formation of cellulose hydrates is apparent.[5]

Concentrated mineral acids form esters or cellulose acids according to the general principles of esterification. With strong

---

[1] Allgemeine Kolloidchemie. See also C. Schwalbe, Zts. Chem. Ind. Koll. 1908, **2**, 217, 229; Zts. ang. Chem. 1908, **21**, 1377; J. S. C. I. 1908, **27**, 278; Chem. Zentr. 1908, **79**, I, 719, 1216; Jahr. Chem. 1905–1908, I, 337; Chem. Ztg. 1908, **32**, 126, 204. A. Klein, Paper, 1919, **24**, 35.

[2] J. prakt. Chem. 1861, **83**, 384; Jahr. Chem. 1861, **14**, 820.

[3] Lands. Versuchs. Stat. **19**, 155; abst. J. C. S. 1876, **30**, 662.

[4] A. Girard, Compt. rend. 1875, **81**, 1105; 1879, **88**, 1322; **89**, 170; Ann. Chim. Phys. 1881, (5), **24**, 337–384; abst. J. C. S. 1879, **36**, 911; 1882, **42**, 378; Jahr. Chem. 1875, **28**, 786; 1879, **32**, 835, 1116; 1881, **34**, 985; Wag. Jahr. 1879, **25**, 419; Ber. 1879, **12**, 2158; 1881, **14**, 2834; Bull. Soc. Chim. 1880, **34**, 507; Mon. Sci. 1879, **21**, 958; Chem. News, 1881, **44**, 216; J. A. C. S. 1879, **1**, 400; Proc. U. S. Nav. Inst. 1882, **8**, 309; Jahr. rein Chem. 1875, **3**, 142; 1881, **9**, 460.

[5] G. Witz, Bull. Rouen, 1881, 342; 1882, 438; Färb. u. Musterztg. **17**, 129; abst. J. S. C. I. 1883, **2**, 378. C. Guignet, Compt. rend. 1889, **108**, 1258; abst. J. S. C. I. 1889, **8**, 1001; J. C. S. 1889, **56**, 847; Chem. Centr.

vitriol, the cellulose-sulfuric acids formed are very unstable, and have, as yet, not been isolated in an undecomposed state. The prolonged action of acids upon cellulose—more readily upon starch—especially upon subsequent dilution with water and boiling, converts the cellulose quantitatively into glucoses, and important manufacturing processes have been established based upon the recognition of this fact.[1]

Concentrated nitric acid produces the corresponding cellulose nitrates, of manifold importance alike in the peaceful and warlike arts. The limit of acid radical substitution appears to be a trinitro derivative, based upon the simple expression of cellulose as a C_6 formula. With organic acids, the esterification is complicated by the phenomena of polymerization subsequent to, concomitant with, or following the normal acetylation process, and in addition the phenomena of hydration occurs, wherein a variable amount of acetic acid is withdrawn from the cellulose ester after the esterification process has been concluded. This "ripening" of the acetated cellulose, whereby the product is rendered soluble in acetone and other desirable solvents, has, as yet, not been satisfactorily explained, notwithstanding the immense amount of painstaking investigation to which the cellulose acetates have necessarily been subjected incident to their employment in such vast quantities as airplane lacquers in the conflict just ended.

The recent researches of H. Dreyfus,[2] L. Lilienfeld,[3] W.

1889, **60**, II, 124; Jahr. Chem. 1889, **42**, 2839; Chem. Ztg. Rep. 1889, **13**, 194; Chem. Tech. Rep. 1889, **23**, I, 145; Wag. Jahr. 1889, **35**, 1180; Ber. 1889, **22**, R, 574; Mon. Sci. 1889, **33**, 986; Chem. News, 1889, **60**, 24.

[1] A. Scheurer, Bull. Soc. Mulhouse, 1888, 364, 399, 439; Mon. Sci. 1889, **33**, 257; abst. J. S. C. I. 1888, **7**, 841, 843; Jahr. Chem. 1889, **42**, 2841; Chem. Tech. Rep. 1888, **27**, II, 60, 105; Chem. Ind. 1889, **12**, 40, 556; Wag. Jahr. 1888, **34**, 1099.

[2] F. P. 462274, 1912; abst. J. S. C. I. 1914, **33**, 248; C. A. 1914, **8**, 3859.

[3] U. S. P. 1188376, 1916; abst. C. A. 1916, **10**, 2145; J. S. C. I. 1916, **35**, 887; Mon. Sci. 1917, **84**, 28; Kunst. 1916, **6**, 282. U. S. P. 1217027, 1217028, 1917; abst. C. A. 1917, **11**, 1545; J. S. C. I. 1917, **36**, 383; Mon. Sci. 1918, **85**, 4. E. P. 12854, 1912; abst. C. A. 1913, **7**, 3839; J. S. C. I. 1913, **32**, 940. E. P. 6035, 1913; abst. C. A. 1914, **8**, 2947; J. S. C. I. 1914, **33**, 417. E. P. 6387, 1913; abst. C. A. 1914, **8**, 2947; J. S. C. I. 1914, **33**, 417; Kunst. 1914, **4**, 236; see also R. Willstaetter, D. R. P. 273800; abst. Kunst. 1914, **4**, 179. E. P. 3370, 1914; abst. J. S. C. I. 1916, **35**, 534. F. P. 447974, 1912; abst. J. S. C. I. 1913, **32**, 420; Mon. Sci. 1914, **80**, 3. F. P. 459972, 1913; abst. J. S. C. I. 1913, **32**, 1153; F. P. 468162, 1914; abst. J. S. C. I. 1914, **33**, 958; D. R. P. 133542, E. Merck; abst. Chem. Centr. 1901, **72**, II, 314; Zts. ang. Chem. 1902, **15**, 739; Jahr. Chem. 1902, **55**, 807; Wag. Jahr. 1 902, **48**, II, 5; Mon. Sci. 1903, **59**, 74. Belg. P. 254591, 1912. Swiss P. 66512. Aust. P. 63526, 1914. Norw. P. 27507.

Suida[1] and W. Denham and H. Woodhouse[2] on the cellulose ethers, have unfolded a hitherto unknown group of bodies, comprising a large number of members which differ from one another in properties according to the number and nature of the alcohols which are linked ether fashion with the cellulose molecule. They result from the replacement of hydroxyl hydrogens in cellulose or its conversion products by alcohol radicals and only await less expensive methods of commercial manufacture for extensive industrial recognition as uninflammable nitrocellulose substitutes, and direct competitors of the more widely known acetylated celluloses. They are white, amorphous powders stable, neutral, soluble in general in the solvents of nitrocellulose and cellulose acetate, the penta-ethylcellulose being most definitely characterized. The combination of esterfication and alkylation in the same cellulose molecule—the acetylation of methylcellulose, or the methylation of formylcellulose—whereby etherfied cellulose esters and esterfied alkylcelluloses result, with their possible industrial applications, apparently is a field, which as yet, has not been approached.

When the celluloses are treated with the alkali hydroxides and carbon bisulfide, solution takes place, the product of cellulose xanthate or sulfocarbonate, under the name of viscose having many industrial applications as in the formation of artificial filaments (wood silk) and described in detail elsewhere in this work.

Properties of the Celluloses. The so-called "true" or "normal" celluloses as obtained from different sources are not identical in chemical and physical deportment, although analytically indistinguishable. Even the highest grade of cotton contains a determinable proportion of material which can only be completely removed by such energetic chemical treatment that the cellulosic

---

[1] Monatsh. Chem. 1905, **26,** 413; Wein. Akad. Ber. 1905, **114,** II b; Färberztg. **16,** 105, 140; abst. J. S. C. I. 1905, **24,** 543; J. C. S. 1905, **88,** 457; Zts. ang. Chem. 1905, **18,** 1990; Chem. Centr. 1905, **76,** I, 1348; Jahr. Chem. 1905–1908, II, 3158; Chem. Ztg. 1905, **29,** 103; Bull. Soc. Chim. 1905, **34,** 971; Meyer Jahr. Chem. 1905, **15,** 512; Rev. gén. sci. 1905, **16,** 239; Rep. de Chim. 1905, **5,** 393; Tschermaks Mitth. **23,** 534; Chem. Zts. 1905, **4,** 444.

[2] J. C. S. 1913, **103,** 1735; 1914, **105,** 2357; abst. C. A. 1914, **8,** 243; 1915, **9,** 203; Chem. Zentr. 1913, **84,** II, 1857; 1915, **85,** I, 81; J. S. C. I. 1913, **32,** 974; 1914, **33,** 1084; Bull. Soc. Chim. 1913, **14,** 1495; Rev. gén. sci. 1913, **24,** 910. See P. Seel, U. S. P. 1281080; abst. C. A. 1919, **13,** 73, for plastic cellulose ethers.

portion is modified, irrespective of how carefully conducted the treatment has been carried on. In the esterification (nitration or acetylation) or alkylation (methylation or ethylation) of cellulose, no definite stages or well-characterized steps are possible, and esters and alkyl derivatives are formed, which analytically imperceptibly blend one into the other, so that, for instance, it is possible to produce by what appears a continuous process, cellulose esters from 6% to 13.5% nitrogen.

And the physical properties and chemical reactions are also not always indicative of well-defined composition, for nitric and acetic esters of cellulose are known, of the same percentage composition, which are or are not soluble in a given solvent or solvent combination. Especially are these differences noticeable in endeavoring to obtain the solvent capacity for a given cellulose ester or compound, where two apparently identical esters, in solution in a known solvent of pre-determined strength and purity may be precipitated from such solutions by entirely different amounts of cellulose ester non-solvents, as benzene or benzine.

The celluloses, when pure are white, amorphous, firm, elastic substances, burning quietly with a luminous, smoky flame. The heat of combustion to CO_2 and H_2O has been given as 4208 calories. G. Fleury[1] has determined the specific heat of some organic substances with the following results: cellulose, 0.366; wool, 0.393; leather, 0.357. In the ordinary moist state, these substances were found to contain 7%, 11%, and 16% of water respectively, and the specific heats in this condition to be: cellulose 0.41; wool, 0.459; leather, 0.45.

Under the term "cellulose," E. Gilson[2] includes the carbohydrates of the membranes which are insoluble in dilute acids or

---

1. Compt. rend. 1900, **130**, 437; abst. J. C. S. 1900, **78**, ii, 188; Chem. Centr. 1900, **71**, I, 680; Jahr. Chem. 1900, **53**, 840; Chem. Ztg. 1900, **24**, 175; Bull. Soc. Chim. 1900, **23**, 340; Rev. Phys. et Chim. 1900, **4**, 117.

2. La Cellule, **9**, No. 2; abst. Chem. Centr. 1893, **64**, II, 530; J. C. S. 1894, **66**, i, 107; J. S. C. I. 1894, **13**, 1106; Jahr. Chem. 1893, **46**, 881; Bull. Soc. Chim. 1894, **11**, 590; Jahr. organ. Chem. 1893, **1**, 265. S. Linder and H. Picton (J. C. S. 1892, **61**, 156; abst. J. S. C. I. 1892, **11**, 64; Chem. Centr. 1892, **63**, I, 367, 516; Ber. 1892, **25**, R, 368; Bull. Soc. Chim. 1895, **14**, 148; Chem. News, 1892, **65**, 47; Chem. Ztg. 1892, **16**, 81, dissolved cellulose in Schweizer's reagent and allowed the clear liquid to settle for several days. The Schweizer's solution itself showed a very feeble luminous beam when a ray of light was passed through it. When the experiment of Tyndal was applied, the cellulose solution showed a well-marked glow when the ray of light was passed through it, the light of the glow being polarized.

alkalis, but soluble in sulfuric acid, and which are colored blue by iodine in the presence of concentrated sulfuric or phosphoric acids. This author has found that if sections of cellular tissue are allowed to remain for a time in contact with Schweizer's reagent, then carefully washed, first with ammonia and then with water so that the copper is dissolved gradually and the cellulose is precipitated slowly, the latter is found in the interior of the cells in the form of nodular or arborescent crystals. These are insoluble in dilute acids and alkalis but soluble in concentrated sulfuric acid, and show also other characteristics of cellulose. To obtain the crystals certain precautions must be observed, one being the complete removal of starch before treatment with Schweizer's reagent. The reaction has been carried out with a large number of phanerogams and cryptogams.

The action of light on cellulose has seldom been studied critically, although the darkening effect which age bestows upon cellulose such as a lace curtain, has been known for some time. G. Witz[1] has examined old curtains, which have been subjected to the action of the sun for thirty years, and by the methylene blue reaction, found the presence of oxycellulose therein. To what extent (if any) this oxidation was accelerated by atmospheric oxygen and the presence of sulfur dioxide or other sulfur compounds was impossible to determine. A. Girard,[2] however, considers that hydrocellulose is more probably produced and that the action of ozone with methylene blue might give analogous color reactions.

In the study of the dry distillation of cellulose, starch and sugar, G. Bantlin[3] has made comparisons by heating them under the same conditions in an iron retort electrically heated. The

---

[1] Bull. Soc. Rouen, 1883, **11**, 169, 188; abst. Jahr. Chem. 1883, **36**, 1782; Wag. Jahr. 1883, **29**, 1068; Mon. Sci. 1884, **26**, 1161. See also H. Schmid, Dingl. Poly. 1883, **250**, 271; abst. J. C. S. 1884, **46**, 528. For reactions of cellulose with iodine, see F. Mylius, Ber. 1895, **28**, 390; abst. J. C. S. 1895, **68**, 313; Chem. Centr. 1895, **66**, I, 792; Jahr. Chem. 1895, **48**, 514; Bull. Soc. Chim. 1895, **14**, 901. For the effect of cellulose hydration on structure, see Sindal and Bacon, Paper, 1919, **24**, 1140.

[2] Ann. Chim. Phys. 1881, (3), **24**, 382; Compt. rend. 1875, **81**, 1105; 1879, **88**, 1322; **89**, 170; abst. J. C. S. 1879, **36**, 911; 1882, **42**, 378; Jahr. Chem. 1875, **28**, 786; 1879, **32**, 835, 1116; 1881, **34**, 985; Wag. Jahr. 1879, **25**, 419; Ber. 1879, **12**, 2158; 1881, **14**, 2834; Bull. Soc. Chim. 1880, **34**, 507; Mon. Sci. 1879, **21**, 958; Chem. News, 1881, **44**, 216; J. A. C. S. 1879, **1**, 400; Proc. U. S. Nav. Inst. 1882, **8**, 309; Jahr. rein Chem. 1875, **2**, 142; 1881, **8**, 460.

[3] J. Gasbeleucht. 1914, **57**, 32, 55; abst. J. S. C. I. 1914, **33**, 129; Chem. Zentr. 1914, **85**, I, 922; C. A. 1914, **8**, 1344.

temperature was raised gradually so as to reach 100° in 1.5 hours, and 500° in 7–8 hours.

The products of distillation in percentage by weight of the dry substance, were as follows:

TABLE II.—DISTILLATION OF CARBOHYDRATES

	Cellulose	Starch	Sugar
Coke	32.9	28.6	12.2
Water	31.7	29.7	6.29
Tar	3.25	2.69	55.04
Acetic acid	3.28	5.29	8.78
Aldehydes	5.82	5.66	6.15
Ketones	0.11	1.11	0.34
Total gases	17.33	22.70	5.96
Carbon dioxide	11.26	13.08	4.37
Ethylene	0.24	0.39	0.05
Hydrogen	0.02	0.03	0.01
Carbon monoxide	4.78	7.64	1.29
Ethane	0.35	0.74	0.11
Methane	0.68	0.82	0.13
Loss or not determined	5.23	4.20	5.38
Composition of tar:			
Carbon	52.20	45.02	38.91
Hydrogen	6.86	6.31	6.19
Oxygen	40.94	48.67	54.90

The time-temperature curves showed that with cellulose an exothermic decomposition takes place between 250° and 300° and that this reaction is complete at 320°. This phenomenon is not shown by starch and sugar. The stability towards heat increases in the order cellulose, starch, sugar, but the first two are more nearly alike in this respect than either is to sugar. Since cellulose does not yield methyl alcohol on dry distillation, it has been supposed that waste sulfite-cellulose lyes contain the constituents of wood which yield valuable distillation products. The lye was therefore partially separated from sulfur compounds by passing through it a current of air and steam, evaporated to dryness, and distilled. A very small yield of liquid products was obtained, and no methyl alcohol, while large quantities of hydrogen sulfide and of mercaptan were evolved.

The sp. gr. of cotton cellulose according to L. Vignon[1] and

---

1. Compt. rend. 1892, **114**, 424; abst. J. S. C. I. 1892, **11**, 1002; Chem. Centr. 1892, **63**, I, 616; Jahr. Chem. 1892, **45**, 2906; Chem. Tech. Rep. 1892, **31**, I, 103; Ber. 1892, **25**, R, 268; Bull. Soc. Chim. 1892, **7**, 247; Mon. Sci. 1894, **39**, 309; Rev. gén. sci. 1892, **3**, 170; Deutsch. Chem. Ztg. 1892, 92.

others is 1.50, although considerable variation often occurs.

In vacuo distillation of cellulose and starch, A. Pictet and J. Sarasin[1] gradually heated pure cotton cellulose under a pressure of 12–15 mm. After the aqueous fractions, there distilled between 200° and 300°, a thick yellow oil which on cooling solidified to a semi-crystalline mass amounting to 45% of the original cellulose, 10% of carbon remaining in the retort. Upon recrystallization from hot water or alcohol, the pasty mass gave white, tabular, anhydrous crystals, m. pt. 179.5°, formula $C_6H_{10}O_5$. The substance was strongly laevorotatory, and could not be distilled under atmospheric pressure without decomposition. From the triacetate (m. pt. 110°) and tribenzoate (m. pt. 199.5°) the material appeared to be identical with the laevoglucosan of C. Tanret,[2] obtained from the glucosides of the Coniferae. This behaves as a trihydric alcohol and yields ordinary dextrose when boiled with dilute mineral acids. In a later paper[3] J. Sarasin proposes for *l*-glucosan a structural formula identical with that put forward by A. Green[4] for the unit complex of cellulose. Sarasin maintains that in the polymerization of *l*-glucosan the middle ring opens, giving two free valencies for the polymerization, because 2.5-dimethylfuran is found among the decomposition products of starch and cellulose. This body does not yield bromomethyl-furfural when treated with Fenton's reagent, and is thus sharply differentiated from cellulose and starch. The author therefore suggests that the middle ring is closed in the case of the glucosan but opens in the polymerized form. There may

---

1. Compt. rend. 1918, **166**, 38; abst. J. S. C. I. 1918, **37**, 49-A; Chem. Zentr. 1918, **89**, I, 1151; J. C. S. 1918, **114**, i, 59; C. A. 1918, **12**, 804. See also J. Sarasin, Arch. Sci. Phys. Nat. 1918, **46**, 5; abst. C. A. 1918, **12**, 2187; J. C. S. 1918, **114**, i, 375. See O. Rau and G. Lambris, J. Gasbeleucht, 1913, **56**, 33; abst. Gas World, 1913, **59**, 259; C. A. 1913, **7**, 3655. H. Hollings and J. Cobb, J. Gasbeleucht, 1914, **57**, 126, 917; abst. Gas World, 1914, **60**, 872; C. A. 1914, **8**, 3110

2. Compt. rend. 1894, **119**, 158; abst. J. C. S. 1894, **66**, i, 564; Chem. Centr. 1894, **65**, II, 360; Jahr. Chem. 1894, **47**, 1112; Chem. Ztg. Rep. 1894, **18**, 194; Ber. 1894, **27**, R, 665; Bull. Soc. Chem. 1894, (3), **11**, 949; Mon. Sci. 1894, **43**, 717; Rev. gén. sci. 1894, **5**, 552; Jahr. organ. Chem. 1894, **2**, 219; Chem. News, 1894, **70**, 72, 282.

3. Helvetica chim. acta, 1918, **1**, 78; abst. C. A. 1918, **12**, 2187; Chem. Zentr. 1918, **89**, II, 711; J. C. S. 1918, **114**, i. 59; Chim. et Ind. 1918, **1**, 279.

4. Zts. Farb. Text. Chem. 1904, **3**, 97; abst. J. S. C. I. 1904, **23**, 382; J. Soc. Dyers Col. 1904, **20**, 117; Zts. ang. Chem. 1904, **17**, 1121; Chem. Centr. 1904, **75**, I, 1069; II, 980; J. C. S. 1904, **86**, i, 652; 1905, **88**, i, 22; Jahr. Chem. 1904, **57**, 1160, 1161; Chem. Ztg. Rep. 1904, **28**, 115; Wag. Jahr. 1904, **50**, II, 398.

or may not be any connection between this simple product of the destructive distillation of cellulose and the observation of C. Cross and E. Bevan[1] that maltol is formed under analogous conditions.[2]

E. Erdmann and C. Schaefer[3] have obtained the following substances by subjecting cellulose to dry, destructive distillation:

(a) Gas containing carbon dioxide, 0.2%; heavy hydrocarbons, 0.5%; oxygen, 0.9%; CO, 65.5%; methane, 19%; H, 11.5%; N, 2.4%.

(b) Aqueous liquid, about 40% of the original cellulose; this forms a reddish brown, strongly acid liquid, of pungent odor, with reducing properties, and gives a deep purple coloration with ferric chloride.

(c) Brown, viscous tar, in amount about 5% of the cellulose. After neutralization with sodium carbonate, and fractional distillation, the aqueous distillate yielded the following products: formaldehyde, furfuraldehyde, maltol,[4] hydroxymethylfurfur-

---

[1] J. Soc. Dyers Col. 1916, **32**, 135; abst. J. S. C. I. 1916, **35**, 628; C. A. 1916, **10**, 2303; J. C. S. 1916, **110**, i, 467.

[2] See E. Vongerichten and F. Müller, Ber. 1906, **39**, 241; abst. J. C. S. 1906, **90**, i, 198; Chem. Centr. 1906, **77**, I, 748; Jahr. Chem. 1905–1908, II, 1948; Bull. Soc. Chim. 1906, **36**, 1145; Rep. de Chim. 1906, **6**, 229.

[3] Ber. 1910, **43**, 2398; abst. J. C. S. 1910, **98**, i, 718; C. A. 1910, **4**, 3223; J. S. C. I. 1910, **29**, 1198; Chem. Zentr. 1910, **81**, II, 1304; Jahr. Chem. 1910, **63**, II, 418; Bull. Soc. Chim. 1911, (4), **10**, 445; Meyer Jahr. Chem. 1910, **20**, 317. It will be recalled that in 1891 (E. P. 19560, 1891; abst. J. S. C. I. 1892, **11**, 939; D. R. P. 64031, 1891; abst. Zts. ang. Chem. 1892, **5**, 499; Chem. Centr. 1892, **63**, II, 1088; Chem. Ztg. 1892, **16**, 1432; 1893, **17**, 1004; Chem. Tech. Rep. 1892, **31**, II, 164; Chem. Ind. 1892, **15**, 485; Wag. Jahr. 1892; **38**, 376; Ber. 1892, **25**, 892; Mon. Sci. 1892, **40**, 166; Indbl. 1892, 358; Meyer Jahr. Chem. 1892, **2**, 362; Tech. Chem. Jahr. 1892–1893, **15**, 169) a patent was issued to H. de Chardonnet for the methodical application of high temperatures for modifying the composition of cellulose materials, in which cotton, lignin or ramie was directed to be heated continuously during 4–8 hours at a constant temperature of 150 to 170 degrees. The cellulose was placed in stoves having shelves composed to tubes through which steam circulated at a pressure of 8–10 atmospheres, air circulation being maintained to regulate the temperature to which the cellulose was exposed. At the conclusion of this heating operation the cellulose is immersed still warm in a nitrating mixture, whereby there is produced a cellulose nitrate of much lower viscosity and greater solubility, so that for the formation of artificial filaments, collodions of as high concentration as 20–25 per cent. of pyroxylin could be produced and spun. See E. Berl, D. R. P. 199885, 1907; abst. C. A. 1908, **2**, 3154; J. S. C. I. 1908, **27**, 937; Zts. ang. Chem. 1908, **21**, 2233; Chem. Zentr. 1908, **79**, II, 466; Meyer Jahr. Chem. 1908, **18**, 309; Chem. Ztg. Rep. 1908, **32**, 382; Wag. Jahr. 1908, **54**, II, 355.

[4] J. Brand, Ber. 1894, **27**, 806; abst. J. C. S. 1894, **66**, i, 270; J. S. C. I. 1894, **13**, 1215; Chem. Centr. 1894, **65**, I, 863; Jahr. Chem. 1894, **47**, 1119; Chem. Ztg. Rep. 1894, **18**, 115; Wag. Jahr. 1894, **40**, 804; Bull. Soc. Chim.

aldehyde and valerolactone, as well as other bodies.

Although Pettenkofer failed to obtain pyrocatechol by the dry distillation of straw and paper, F. Hoppe-Seyler[1] upon heating Swedish filter paper at 200° for 4 to 6 hours along with water in a sealed tube, obtained formic acid and pyrocatechol. This body was also yielded by starch, cane sugar and milk sugar by the same treatment.

P. Klason, G. v. Heidenstam and E. Norlin[2] have also investigated the products obtained by the dry distillation of cellulose obtained from various sources. They found that the velocity of charring action begins to become considerable at

1894, **12**, 1096; Mon. Sci. 1895, **45**, 63; Jahr. organ. Chem. 1894, **2**, 671; Meyer Jahr. Chem. 1894, **4**, 261. H. Kiliani and M. Bazlen, Ber. 1894, **27**, 3113; abst. J. C. S. 1895, **68**, i, 80; J. S. C. I. 1895, **14**, 378; Chem. Centr. 1895, **66**, I, 27; Chem. Ztg. Rep. 1894, **18**, 306; Wag. Jahr. 1894, **40**, 904; Jahr. Chem. 1894, **47**, 1120; Bull. Soc. Chim. 1895, **14**, 500; Tech. Chem. Jahr. 1894–1895, **17**, 286; Meyer Jahr. Chem. 1894, **4**, 261. A. Peratoner and A. Tamburello, Giorn. Sci. Nat. Econ. **25**, 272; Gaz. chim. ital. 1906, **36**, I, 33; abst. J. C. S. 1905, **88**, i, 807; Chem. Centr. 1905, **76**, II, 680; Jahr. Chem. 1905–1908, II, 3814; Meyer Jahr. Chem. 1905, **15**, 213; Rep. de Chim. 1906, **6**, 276. See also, Ber. 1903, **36**, 3407; abst. J. C. S. 1904, **86**, i, 61; J. S. C. I. 1903, **22**, 1265; Chem. Centr. 1903, **74**, II, 1020; Chem. Ztg. Rep. 1903, **27**, 326; Bull. Soc. Chim. 1904, **32**, 819. F. Bergius, J. S. C. I. 1913, **32**, 462; abst. C. A. 1914, **8**, 1004; J. C. S. 1913, **104**, ii, 579; Chem. Zentr. 1913, **84**, II, 932; Mon. Sci. 1913, **78**, 664; Rev. gén. sci. 1913, **24**, 452. H. Suringar and B. Tollens, Zts. ang. Chem. 1896, **9**, 749; abst. J. C. S. 1897, **72**, ii, 235; Chem. Centr. 1897, **68**, I, 199; Jahr. Chem. 1896, **49**, 2281; Chem. Ztg. Rep. 1897, **21**, 27. Grosseteste and A. Scheurer, Bull. Soc. Ind. Mulhouse, 1883, 65, 68; abst. Wag. Jahr. 1883, **29**, 1052; Mon. Sci. 1883, **25**, 40, 139. G. Buettner and H. Wislicenus, J. prakt. Chem. 1909, (2), **79**, 194; abst. C. A. 1910, **4**, 1235; J. S. C. I. 1909, **28**, 417; J. C. S. 1909, **96**, i, 290; Zts. ang. Chem. 1909, **22**, 1514; Chem. Zentr. 1909, **80**, I, 1518; Jahr. Chem. 1909, **62**, II, 33; Meyer Jahr. Chem. 1909, **19**, 324; Bull. Soc. Chim. 1910, **8**, 242.

[1] Ber. 1871, **4**, 15; abst. J. C. S. 1871, **24**, 226; Chem. Centr. 1871, **42**, 84; Bull. Soc. Chim. 1871, **15**, 98; Chem. News, 1871, **23**, 131; Jahr. Chem. 1871, **24**, 476. A. Scheurer, Bull. Soc. Mulhouse, 1888, 361, 399, 439; Mon. Sci. 1889, **33**, 257; abst. J. S. C. I. 1888, **7**, 841, 843; Jahr. Chem. 1889, **42**, 2841; Chem. Tech. Rep. 1888, **27**, II, 60, 105; Chem. Ind. 1889, **12**, 40, 556; Wag. Jahr. 1888, **34**, 1099. H. Ost and F. Westhof, Chem. Ztg. 1909, **33**, 197; abst. C. A. 1909, **3**, 1394; J. S. C. I. 1909, **28**, 325; J. C. S. 1909, **96**, i, 210; Ztg. ang. Chem. 1909, **22**, 1856; Chem. Zentr. 1909, **80**, I, 1231; Jahr. Chem. 1909, **62**, II, 385; Wag. Jahr. 1909, **55**, II, 514; Bull. Soc. Chim. 1909, (4), **6**, 685; Rep. de Chim. 1909, **9**, 321. P. Klason, Wochenbl. Papierfab. 1898, **29**, 2176; Pap. Ztg. 1898, **23**, 528; Ber. 1900, **33**, 2343; Pap. Fab. 1900, **7**, 26, 445, 627, 671, 701, 796; Pap. Ztg. 1909, **34**, 996, 1315; 1910, **35**, 2116; Zts. ang. Chem. 1909, **22**, 1205, 1423; Wochenbl. Papierfab. 1909, **40**, 2668; Chem. Ztg. 1906, **30**, 770.

[2] Arkiv. Kem. Min. Geol. 1908, **3**, 1; abst. J. C. S. 1908; **94**, i, 717; C. A. 1908, **2**, 3280; J. S. C. I. 1909, **28**, 132; Zts. ang. Chem. 1909, **22**, 1205; Chem. Zentr. 1909, **80**, I, 109; Jahr. Chem. 1905–1908, II, 4749; Meyer Jahr. Chem. 1909, **18**, 302; Chem. Ztg. Rep. 1908, **32**, 252, 602; Wag. Jahr. 1908, **54**, II, 20; Bull. Soc. Chim. 1909, (4), **6**, 1152.

about 270°, at which temperature the dry distillation of cellulose is an exothermic process, the heat of the reaction being about 6% of the heat of combustion of cellulose. The gases evolved during the distillation were found to possess a heating value of about 3.5% of the heat of combustion of the cellulose, and include hydrogen and aromatic hydrocarbons. They found the lignocelluloses yielded more acetic acid than cotton cellulose.

According to H. Hofmann[1] sulfite cellulose and paper undergo a chemical change upon being dried, which begins at about 90°, increases considerably above 100°, and is dependent upon the temperature and the time of heating. This change renders the cellulose easily attacked by acid, but the sugar obtained from it is the same as before, i. e., xylose.[2]

Upon boiling with water, pure cellulose yields little or no sugar, but under a pressure of 10 atmospheres, the amount of sugar may rise to as high as 13.5% of the cellulose boiled.[3] By heating with water in a closed tube to 200°, the cellulose breaks down and forms a dark brown solution with the production of formic acid,[4] and by solution of alkali from the glass composing the tube, small amounts of pyrocatechol and protocatechuic acid are formed. When the glass is replaced by platinum[5] these products cannot be found.

When cellulose is heated with barium hydroxide to 150°–180° fermentation lactic acid is formed together with small quantities of formic, propionic, oxalic, oxybutyric and glycollic acids.[6] With ammonia and calcium chloride, heating for six hours at 100° transforms the cellulose into an amidized cellulose,[7] which

---

1. Papier Ztg. 1906, **31**, 4331; abst. C. A. 1907, **1**, 486; Wochenbl. Papierfabr. 1907, **38**, 1289.

2. H. Hofman, Papier Ztg. 1907, **32**, 2558; abst. C. A. 1907, **1**, 2634; J. S. C. I. 1907, **28**, 942.

3. H. Tauss, Dingl. Poly. 1889, **273**, 276; abst. J. S. C. I. 1890, **9**, 883; Chem. Centr. 1889, **60**, II, 444; Jahr. Chem. 1889, **42**, 2838; Chem. Ztg. Rep. 1890, **14**, 232; Chem. Tech. Rep. 1890, **29**, II, 105; Chem. Ind. 1889, **12**, 514; Wag. Jahr. 1889, **35**, 1; Ber. 1889, **22**, R, 769; Mon. Sci. 1890, **35**, 164; Chem. News, 1890, **61**, 169.

4. F. Hoppe-Seyler, Ber. 1871, **4**, 15; abst. J. C. S. 1871, **24**, 226; Chem. Centr. 1871, **42**, 84; Jahr. Chem. 1871, **24**, 476; Bull. Soc. Chim. 1871, **15**, 98; Chem. News, 1871, **23**, 131.

5. F. Hoppe-Seyler, Zts. physiol. Chem. 1889, **13**, 73.

6. P. Schuetzenberger, Jour. Pharm. Chim. 1877, **25**, 141.

7. L. Vignon and L. Casella & Co., D. R. P. 57846, 1890; abst. Zts. ang. Chem. 1891, **4**, 560; Chem. Centr. 1892, **63**, I, 80; Chem. Tech. Rep. 1891, **30**, II, 119; Wag. Jahr. 1891, **37**, 1121; Ber. 1892, **25**, R, 139; Indbl.

enhances its affinity for dyestuffs. Patterns may thus be executed for differential dyeing in calico printing.

Viscosity of Cellulose Solutions. H. Ost[1] has made a number of viscosity determinations of cuprammonium solutions of various forms of cellulose such as cotton, wood pulp, filter paper, etc., which has led to the conclusion that viscosity determinations supply useful information as to the nature and technical value of cellulose.

The cuprammonium solution used was prepared by treating a solution containing 59 gm. copper sulfate with ammonium hydroxide, and dissolving the basic copper sulfate thus obtained in ammonium hydroxide of sp. gr. 0.90 to form one liter of solution. A quantity of cellulose was dissolved in this solution in each case to correspond with one gram of the anhydrous cellulose in 50 cc. The viscosity was determined in a special form of Ostwald's capillary viscometer. It has been established that previous treatment of the cellulose with bleaching agents produces a marked decrease in viscosity of the cuprammonium solution, the same result also being brought about by heating cellulose for about 15 hours at 120°-125°. On the other hand, treatment of the cellulose with a cold 5% solution of sodium hydroxide for about 24 hours, or with a cold 20% solution for one hour, does not affect the viscosity of the solution.

From this observation the conclusion is drawn that cotton does not undergo a chemical change during mercerization. NaOH however, does exert a chemical action on cotton—although the action is a very slow one—because cotton which has been soaked in a 20% solution of sodium hydroxide, pressed, and kept in a stoppered bottle for several months, dissolves very readily in a cuprammonium solution, and the solution possesses a low viscosity.

Cuprammonium solutions of hydrocellulose obtained by the action of dilute mineral acids on cellulose, are much less viscous than equivalent weight solutions of cellulose which previously have been acted upon by bleaching agents. The commercial

---

1891, 382; Tech. Chem. Jahr. 1891-1892, **14**, 485. See also Compt. rend. 1891, **112**, 487; abst. Bull. Soc. Chim. 1891, (3), **5**, 472; Jahr. Chem. 1891, **44**, 2814; Chem. Ztg. Rep. 1891, **15**, 76.

[1] Zts. ang. Chem. 1911, **24**, 1892; abst. Kunst. 1911, **1**, 452; J. C. S. 1911, **100**, i, 838; J. S. C. I. 1911, **30**, 1247; Chem. Zentr. 1911, **82**, II, 1518; Meyer Jahr. Chem. 1911, **21**, 220; C. A. 1912, **6**, 684.

application of the viscosity test to cellulose is given at the close of this chapter.

Optical Properties of Cellulose. In his polarimetric investigations of various forms of cellulose, A. Levallois[1] prepared the latter by the action of ferrous chloride solution on guncotton and on pyroxylin, which were then dissolved in a cuprammonium solution and the rotatory power of this solution compared with that of a similar solution of pure cellulose from paper, with the following results:

	Deviation
Pure cellulose	9.5°
Cellulose from trinitrocellulose	8.5°
Cellulose from pyroxylin	8.5°

The differences observed were attributed by Levallois to hydration produced by prolonged washing of the reduced cellulose with HCl. Similar determinations were made with a cuprammonium solution of cellulose which had been immersed in sulfuric acid of a predetermined strength for a definite period of time. In the first series the acid was of 66° Bé. strength diluted with its own volume of water, whereas in the second series the same acid was diluted with only half its volume of water.

First series		Second series	
		Immersed 10 seconds	8.8
		Immersed 30 seconds	9.5
Immersed 1 minute	9.5	Immersed 1 minute	9.0
Immersed 5 minutes	8.7	Immersed 5 minutes	9.0
Immersed 15 minutes	8.7	Immersed 15 minutes	8.8

The above results are practically identical. As A. Bechamp has shown,[2] the cellulose is converted into a pasty mass by the acid, which is entirely dissolved in about 5 minutes. The solu-

---

[1] Compt. rend. 1884, **98,** 732; **99,** 43, 1027; abst. J. C. S. 1884, **46,** 577, 1288; Bull. Soc. Chim. 1885, **43,** 83; Ber. 1884, **17,** R, 206, 427; 1885, **18,** 64; Jahr. Chem. 1884, 302, 303; Mon. Sci. 1884, **26,** 199; Chem. News, 1884, **49,** 124, 190; **50,** 79; 1885, **51,** 147. H. Ambronn, Zts. Chem. Ind. Koll. 1913, **13,** 200; abst. J. S. C. I. 1913, **32,** 991; C. A. 1914, **8,** 422; Chem. Zentr. 1913, II, 1275; J. C. S. 1913, **104,** ii, 897; Wag. Jahr. 1913, I, 457.

[2] Compt. rend. 1884, **99,** 1027, 1122; 1885, **100,** 117, 279, 368, 456; abst. Ber. 1885, **18,** 113; Chem. News, 1885, **51,** 117; Jahr. Chem. 1884, 303; Mon. Sci. 1885, **27,** 88; Bull. Soc. Chim. 1885, **43,** 611; J. C. S. 1885, **48,** 237. C. Naegeli, Ber. d. Bayer Akad. 1862, I, 307; abst. Instit. 1863, 263; Jahr. Chem. 1863, 571.

tion is at once precipitated if poured into alcohol, and when dried forms a friable mass slightly soluble in water, and very soluble in cuprammonium solution. The latter solution, however, has only about half the rotatory power of a cuprammonium solution of pure cellulose.

According to W. Harrison[1] double refraction in textile fibers is due to the presence of internal stresses, and may be increased by compressing the fibers, for instance, between a thick glass plate and a grooved celluloid film placed on a second glass plate, the whole being examined on the stage of a microscope in polarized light between crossed nicols and the difference between the compressed and uncompressed portions noted. Examined in this way under a pressure of 5 tons per sq. in., wool fibers showed interference figures indicating spreading of the fiber substance in all directions away from the center of pressure; cotton fibers offer greater resistance to deformation than wool fibers and show no interference figures.

After removal of the pressure, in both cases, the fibers did not return to their original shape; the increased double refraction of the compressed portions remain until the stresses are relieved by immersion in water. The return to the original shape in cold water is much more rapid in the case of wool than in that of cotton. Similar results were obtained when fibers which had been bent or twisted were placed in cold water. Fibers subjected to a limited amount of extension when dry do not return to their original length when kept loose in a dry atmosphere, but do so rapidly when placed in the water; the effect of a humid atmosphere is the same as that of cold water but much less rapid.

At high temperatures, water renders fibers truly plastic; deformation is produced by compression, but this causes little or no internal stresses. These experiments have a bearing on the "feel" and finish of textile fabrics. The double refraction shown by cotton fibers in the natural state is due to permanent strain produced by internal stresses; it disappears when the fiber is

---

[1] Proc. Roy. Soc. 1918, A-**94**, 460; abst. J. S. C. I. 1918, **37**, 460-A; C. A. 1918, **12**, 1928; Ann. Rep. Soc. Chem. Ind. 1918, **3**, 116. See also W. Harrison, J. Text. Inst. 1916, **7**, 233; abst. C. A. 1917, **11**, 233. According to J. Larguier des Bancels, Compt. rend. 1909, **149**, 316; C. A. 1911, **5**, 2333; J. C. S. 1909, **96**, ii, 720; Chem. Zentr. 1909, II, 1297; Jahr. Chem. 1909, 1055. See also J. Larguier des Bancels, Compt. rend. 1903, **136**, 1388; abst. Chem. Centr. 1903, II, 175. The electric charge of cotton fibers is negative.

swollen by cuprammonium solution, except in those bands where swelling has not occurred. The direction of strain is parallel to the axis of the fiber and the natural condition of cotton fibers correspond with that produced by tension on an elastic body; all the other natural fibers appear to be subject to similar stresses. The shrinkage in length which takes place on mercerization appears to be due to the balancing of the internal stresses. The condition of a highly nitrated cotton fiber containing more than 12.5% of nitrogen is just the reverse and corresponds to that produced in an elastic body by compression in the direction of the axis.

In both cotton and wool the distribution of the internal stresses is irregular. The modification of the internal stress produced by boiling wool in water is similar to that produced by treating cotton fibers with concentrated alkali. Cold water has no influence in relieving the natural stresses, probably because these are due to changes in volume, whereas stresses caused by external compression are only due to changes in shape. Artificial fibers are generally produced with internal stresses which cause double refraction, similar to those occurring in natural cotton, and the physical forces which are operative in the formation of artificial fibers from viscous fluids are analogous to those acting in the formation of natural fibers from plastic cell materials.

J. Koenig and F. Huehn[1] have determined the specific rotatory power of different types of cellulose, 0.5 gm. of the previously dried cellulose being dissolved in zinc chloride, the solution being finally made up to 25°. The measurements were made at 18°, but were rendered difficult by the opacity of the solutions. The solutions presented the phenomena of multi-rotation, indicated in the following table:

[1] Zts. Farbenind. **5**, 80; **6**, 102. The preparation and drying of the various celluloses used are given in the original article. Behrens "Anleitung zur Mikrochemischen Analyse," has studied dichroism on dyed fibers and has noticed it much less with cotton fiber than with flax, hemp and ramie. C. Schwalbe, abst. J. Soc. Dyers Col. 1920, **36**, 26, in an investigation of hydro- and oxy-celluloses from wood cellulose, has found that these products, in common with naturally occurring degradation products of cellulose such as cellulose, dextrin and the hemicelluloses, are converted into mucilage by mechanical means, and particularly by pressure. This mucilage is converted into an irreversible colloid on drying, which has lost the property of swelling in an atmosgphere saturated with water vapor.

TABLE III.—SPECIFIC ROTATORY POWER OF DIFFERENT TYPES OF CELLULOSE

Material	Observer	Time in Hours		Specific Rotation $[\alpha]^{18}_{D}$
		h	m	
Raw cotton fiber	König	0	15	0
		72	15	80.03
		112	15	80.03
Cotton cellulose	König		15	0
		72	30	82.55
		92	30	80.40?
Cotton cellulose	Tollens	1		2.92
		78		72.02
		94	30	69.15?
Cotton cellulose	Cross and Bevan	4		13.17
		73		53.57
		76		53.42
Jute cellulose	König	1	30	4.28
		56	30	71.50
		71	30	66.92
Jute cellulose	Tollens	1	30	6.57
		49		71.57
		61		45.91?
Swedish filter paper	Munktell		30	0.27
		107		66.15
Dissolved cold		124		62.69?
Same, dissolved hot			30	59.25
		5		69.21
		71		52.22?
Absorbent cotton (dissolved cold)		6	30	18.21
		78	30	71.45
		99		58.84?
Same, dissolved hot			30	41.59
		47		71.65
		75	30	60.59?
Cotton hydrocellulose	Girard		30	1.06
		15		39.73
		34		45.02?
		31		37.08?
Oxycellulose	Vignon		30	3.98
		30		52.29
		45		40.00?

TABLE III (*continued*)

Material	Observer	Time in Hours		Specific Rotation $[\alpha]^{18}_{D}$
		h	m	
Oxycellulose	Vignon and von Hauff		45	0.80
		54		44.84
		71	30	37.00?
Spruce cellulose	König		30	10.35
		71	30	60.51
		78		57.02
Beech cellulose	König		15	0.27
		31		60.33
		47		59.24?
Glucose	Schuchardt-Gorlitz			60.0
Xylose	Schuchardt-Gorlitz			32.0

W. Hartley[1] has recorded that cellulose in the form of white blotting paper is fluorescent and capable of rendering visible the whole of the ultra-violet spectrum as far as wave length 2000. S. Lewis[2] has continued these studies and photographically recorded the relative intensity of the degradation of ultra-violet light at various wave lengths to visible rays capable of passing through glass and affecting the photographic plate. His general results show that the power and distribution of the fluorescent properties are definite functions of the chemical constitution, and their variations conform to what is known of the influence of substituent groups on the properties of the original substance.

Normal cellulose, from whatever source it is derived, gives a fairly uniform spectrum, but the intensity varies with the specimen under obeservation. The cellulose from rhubarb stalk

---

[1] J. C. S. 1893, **63**, 245; Chem. News, 1892, **66**, 298; abst. Chem. Centr. 1893, I, 76; Meyer Jahr. Chem. 1892, **2**, 11.

[2] J. Soc. Dyers Col. 1918, **34**, 167; abst. J. S. C. I. 1918, **37**, 542-A. For the ultramicroscopic behavior of cellulose, consult N. Gaidukow, Färb. Ztg. 1907, **18**, 392; Zts. Farbenind. **7**, 251, 267; Ber. Botan. Ges. 1907, **24**, 581; Zts. ang. Chem. 1908, **21**, 393; Chem. Zentr. 1907, I, 643; 1908, I, 1217; Jahr. Chem. 1905-8, II, 3181; Bull. Soc. Chim. 1908, (4), **4**, 637. Compare G. Quincke, Pogg. Ann. 1861, **93**, 513; Bibl. Univ. Archives, 1862, **13**, 185; Nuovo Cimento, 1862, **15**, 29.

and cuticle falls in the same group. Modified celluloses, such as viscose fabric and parchmentized paper, show a considerable divergence from the normal; well beaten "bank" paper falls in the same class, which is characterized by a strong effect at a wavelength of 2750. Ground wood paper (lignocellulose) is devoid of fluorescent properties, and the cellulose nitrates are nearly, if not quite, inactive.

On the other hand, the acetylcelluloses exhibit a fluorescence which is generally much stronger than that of the normal cellulose, and which is much stronger toward the visible region than toward the extreme ultra-violet. For media of the same chemical constitution the resulting degraded spectrum is much the same for the transparent film through which the ultraviolet light is transmitted as for the opaque network in which it is reflected at the surface of the fibers.

Cellulose and Heat. At ordinary atmospheric temperatures, the celluloses appear to be stable for an indefinite period if kept dry unless decomposition processes are started by the presence of ferments, molds or bacteria. This has been proven conclusively in the examination of paper of hundreds if not thousands of years old. The resistance against the action of the air is exceedingly great.

According to Bowman, cellulose, like animal charcoal, possesses the function of condensing upon its surface large quantities of oxygen. The normal hygroscopic moisture present in cellulose gradually escapes upon heating, but if this heating is carried out in a partial vacuum it is possible to dry it to constant weight—cotton cellulose at 30–40 degrees—although temperatures of 70°–90° are more effective. It would appear that the dehydration of cellulose in a cathode ray vacuum has as yet not been attempted. Prolonged drying, however, causes again an appreciable increase in weight, either due to a gradual decomposition of the cellulose itself or more rationally to a decomposition of the impurities in the cellulose fiber. It has been assumed that prolonged heating leads to a gradual oxidation, but it appears more probable that the oxycellulose formed during the bleaching process is the cause of this increase in weight during this heating. It has long been known that certain oxycelluloses undergo decomposition at 100°

whereby they become yellow,[1] and tend to eventually disintegrate.

The changes in cellulose observed by E. Winterstein[2] apparently were made upon a material containing relatively large amounts of oxycellulose. On heating cellulose (cotton) to 110°, W. Schramm[3] and A. Schweizer[4] observed on the thermometer surrounded by a mass of fibers, a rise in temperature of 9°. Such a rise in temperature is not infrequent with cotton waste containing fat or other readily oxidizable impurities.

F. Cohn[5] and Kraut[6] have been able to only partially corroborate this.

Drying of cotton is stated to reduce the strength, this weakening in the opinion of some[7] being due to the presence of traces of acid which forms hydrocellulose, whereby the strength is reduced. This assumption has been doubted by other investigators. The affinity of dyes for cotton shows in a marked degree that drying produces changes in the nature of the cellulose.

J. Hübner[8] and E. Knecht[9] have pointed out that cotton dried at 100° absorbs moisture from the air, wherefore it is difficult to obtain uniform absorption. For instance, absorbent cotton loses its principal property of absorption if over-dried.[10] However, the property of absorbing acids also seems to be affected by excessive drying. In general, therefore, it is always preferable to dry at as low a temperature as is consistent, especially for cotton intended for subsequent nitration. After cellulose has been dried at 100°-110° and is then further heated to 150°, it loses more water, but on cooling to 110° this amount of water is

---

[1] C. Schwalbe, Zts. ang. Chem. 1908, **21**, 1322; abst. Chem. Zentr. 1908, II, 447; C. A. 1908, **2**, 2448; J. C. S. 1908, **94**, ii, 627; Bull. Soc. Chim. 1909, **6**, 58; Jahr. Chem. 1905-8, II, 960; Meyer Jahr. Chem. 1908, **18**, 504.

[2] Zts. Physiol. Chem. 1892, **17**, 391; abst. Jahr. Chem. 1892, 2475; J. C. S. 1893, **64**, i, 127; Chem. Centr. 1893, I, 22.

[3] Zts. ang. Chem. 1908, **21**, 254; abst. Chem. Zentr. 1908, I, 1217; J. S. C. I. 1908, **27**, 221; Bull. Soc. Chim. 1908, **4**, 634; Chem. Ztg. Rep. 1908, **32**, 137.

[4] Leipziger Monatschrift. f. Text. Ind. 1908, **23**, 139; abst. Chem. Ztg. Rep. 1908, **32**, 436.

[5] Ber. botan. Ges. 1893, **11**, 66.

[6] Chem. Ztg. 1893, **17**, 1388.

[7] Wochenblatt, 1905, **36**, 3498, 3737; 1908, **37**, 88.

[8] J. S. C. I. 1909, **28**, 644; abst. Chem. Zentr. 1909, II, 1284; C. A. 1910, **4**, 1241; Bull. Soc. Chim. 1910, **8**, 59; Zts. ang. Chem. 1909, **22**, 1120.

[9] J. Soc. Dyers Col. 1908, **24**, 67, 68; abst. J. S. C. I. 1908, **27**, 400; Chem. Ztg. Rep. 1908, **32**, 272; Wag. Jahr. 1908, II, 467.

[10] Zts. ges. Text. Ind. 1909, **12**, 780.

again regained.[1] The water given off at 100° has been designated as "water of constitution," but experiments made by C. Schwalbe[2] to effect dehydration of the cellulose with toluol or xylol gave at first an excessive water in the case of the hydratcelluloses and mercerized cellulose. Later experiments with larger quantities showed no difference between mercerized cotton and ordinary cotton, regarding the readiness of dehydration. These results were confirmed by H. Ost and F. Westhoff,[3] the latter investigators being of the opinion that complete expelling of the hygroscopic moisture requires temperatures of 120° to 125°, they recommending that the heating be done in a current of hydrogen or carbon dioxide.

According to the investigations of A. Scheurer,[4] decomposition of cellulose commences at 140° to 150°. The effects of the heating of cotton fabrics to these temperatures has been further studied by Grosseteste, who observed but a slight yellowing at 150° and a decrease in the tensile strength of the fabric, while at 210° the cellulose became brown and very weak. The duration of the heating of the boiled raw cotton fabric to 180° reduces the strength which originally was 16 to 17, while two hours heating at the same temperature brought the value down to 15; four hours to 13; 8 hours to 8.75. The resistance, therefore, of cotton towards heat depends primarily upon the duration of the time to which it is exposed.

C. Koechlin[5] found that when cotton was exposed for several months to the temperature of steam pipes, through which steam of two to three atmospheres circulated and which therefore was of the temperature of about 120° to 130°, the cotton was com-

---

[1] Schweizer, Leipz. Mon. Text. Ind. 1908, **23**, 139; abst. Chem. Ztg. Rep. 1908, **32**, 435.

[2] Zts. ang. Chem. 1908, **21**, 1321; abst. Chem. Zentr. 1908, II, 447; C. A. 1908, **2**, 2448; J. C. S. 1908, **94**, ii, 627; Bull. Soc. Chim. 1909, **6**, 58; Jahr. Chem. 1905–8, II, 960; Meyer Jahr. Chem. 1908, **18**, 504.

[3] Chem. Ztg. 1908, **33**, 197; abst. J. S. C. I. 1909, **28**, 325; J. C. S. 1909, **96**, i, 210; Chem. Zentr. 1909, I, 1231; C. A. 1909, **3**, 1394; Zts. ang. Chem. 1909, **22**, 1856; Rep. de chim. 1909, **9**, 321; Bull. Soc. Chim. 1909, **6**, 685; Meyer Jahr. Chem. 1908, **18**, 504.

[4] A. Scheurer, Bull. Soc. Mulhouse, 1883, **53**, 68; abst. Mon. Sci. 1883, **25**, 139. See also Dingl. Poly. 1885, **255**, 349; abst. J. S. C. I. 1885, **4**, 340.

[5] Bull. Soc. Mulhouse, 1888, **55**, 547; abst. Mon. Sci. 1888, **31**, 509, 1385; J. S. C. I. 1888, **7**, 841; Chem. Ind. 1888, **11**, 400; 1889, **12**, 15; Chem. Tech. Rep. 1888, I, 37, 71; II, 60; Chem. Ztg. 1888, **12**, 375; Jahr. Chem. 1888, 2859.

pletely carbonized, and insoluble in all simple or mixed solvents.

The action of heat and dry and moist air, has also been studied by A. Scheurer[1] who found that at 140° the strength of a piece of cotton fabric is but little affected in the presence of water and pressure, while at 150° to 160° a material reduction in the strength appears. Dry, hot air, if anything, is more dangerous.

According to C. Bartsch[2] both dry and moist air readily injures paper. The German patent of H. de Chardonnet[3] for the preparation of cotton preliminary to nitration, advocates among other things, heating cotton to 180°, upon the assumption that this temperature leads to favorable changes in the molecule. A refinement of this crude method has been recommended by E. Berl[4] for the purpose of preparing material especially suitable for the manufacture of guncotton. Berl considers the process to be that of depolymerization.

The heating of cotton cellulose in indifferent gases has been described by Cross and Bevan.

Bowman states that upon the heating of cellulose, and especially cotton, to temperatures above 100°, as long as no carbonization of the fiber occurs, the temperature may with safety reach 112° to 114°. J. Matthews,[5] however, considers that de-

---

[1] Bull. Soc. Mulhouse, 1893, **62**, 89; abst. J. S. C. I. 1893, **12**, 1025; Wag. Jahr. 1893, **39**, 999; Färberztg. 1892, **4**, 290; Meyer Jahr. Chem. 1893, **3**, 519.

[2] Mitt. Kgl. Materialprüfungsamt, 1909, **27**, 138; abst. Chem. Zentr. 1909, II, 850; Papierfabr. 1909, **8**, 774; Zts. ang. Chem. 1909, **22**, 2205; Chem. Ztg. Rep. 1909, **33**, 450; C. A. 1909, **3**, 2871.

[3] D. R. P. 64031, 1891; abst. Wag. Jahr. 1892, **38**, 376; Ber. 1892, **25**, 699; Zts. ang. Chem. 1892, **5**, 499; Chem. Centr. 1892, II, 1088; Meyer Jahr. Chem. 1892, **2**, 362; Tech. Chem. Jahr. 1892, **15**, 169; Chem. Ztg. 1892, **16**, 1432; 1893, **17**, 1004; Chem. Tech. Rep. 1892, II, 164; Chem. Ind. 1892, **15**, 485; Mon. Sci. 1892, **40**, 166; Indbl. 1892, 358.

[4] D. R. P. 199885, 1907; abst. Zts. Schiess. Sprengs. 1909, **4**, 81; Mon. Sci. 1911, **74**, 93; Zts. ang. Chem. 1908, **21**, 2233; Chem. Zentr. 1908, II, 466; Chem. Ztg. Rep. 1908, **32**, 382; Chem. Ind. 1908, **31**, 454; J. S. C. I. 1908, **27**, 937; Wag. Jahr. 1908, II, 355.

[5] "Textile Fibres" page 147. H. Pringsheim and H. Magnus (Zts. physiol. Chem. 1919, **105**, 179; abst. J. S. C. I. 1919, **38**, 714-A; J. C. S. 1919, **116**, i, 473) have determined the acetyl content of lignin, determining that the acetic acid formed from wood products by treatment with caustic alkalis. C. Scagliarini and T. Minganti (Annali Chim. Appl. 1919, **12**, 52; abst. J. S. C. I. 1919, **38**, 810-A) have studied the products of distillation of hemp waste. Samples distilled inan iron laboratory retort between 350° and 400° C. yielded gas containing CO_2, 26.3; CO, 25.5; CH_4, 8.0, and H_2, 14.0%. The liquid products consisted of 50.8% of pyroligneous acid, with traces of

hydration occurs when cellulose is heated to 160° in either dry or wet air and is accompanied by a destruction of the structure. Will was unable to find a difference as to the water absorption of Texas cotton in samples dried at 170° and those dried at 40°. Where cellulose is heated to temperatures above 200° it is gradually decomposed with the evolution of gases.

According to P. Klason, G. von Heidenstam and E. Norlin,[1] who studied this process very minutely, no substantial amount of gases are evolved on heating cellulose between 100° and 260°, but that the gas evolution becomes a substantial one at the real reaction temperature of 270°. Towards the end of the reaction, carbon monoxide gas is generated and the carbon dioxide content falls to 50%; finally only methane is evolved. The gas evolution is very sensitive against variation of temperature; accidental rise in the temperature materially increases the gas evolution. Expressed in volume per cents., the composition of the gases, if they are formed from hydrogen and aromatic hydrocarbons, is

CO_2	57.87%
C_2H_4	1.53%
CO	36.37%
CH_4	4.23%
	100.00%

According to a previous investigation of E. Chorley and W. Ramsay,[2] the gases contain a small amount of free oxygen. Liquid products are also liberated in addition to the gases as has been determined by E. Chorley and W. Ramsey, who have found the following:

ammonia, a small amount of methyl alcohol, and from 5% to 6% of tar. The tar was composed of 57.55% of water, 2.35% of an oil distilling at 100°. 1.09% at 100° to 170° C., 14.50% at 170° to 230° C., and 24.47% of residue. The solid products consisted of 57.02% of charcoal containing 5.10% of ash. The charcoal is porous, and has pronounced decolorizing properties. In the phenomenon of wood drying, H. Tiemann (J. Frank. Inst. 1919, **188**, 27; abst. J. S. C. I. 1919, **38**, 863-A) has given an account of the internal stresses which occur in wood during the progress of drying from the green condition, and the relationship between them is mathematically shown.

---

[1] Zts. ang. Chem. 1909, **22**, 1205; 1910, **23**, 1252; Arkiv. för Kemi. Min. Geol. 1908, **3**, No. 10, 1; abst. Chem. Zentr. 1909, I, 110; J. S. C. I. 1909, **28**, 132; see also abst. J. C. S. 1908, **94**, i, 717, 955; C. A. 1908, **2**, 3280; 1909, **3**, 1810; 1910, **4**, 1803, 3135; Chem. Ztg. Rep. 1909, **33**, 435.

[2] J. S. C. I. 1892, **11**, 395, 872; abst. Jahr. Chem. 1892, 2897, 2898; Chem. Centr. 1893, I, 189; Chem. Ztg. 1893, **17**, 653, 1709. See also Cross and Bevan, "Cellulose," page 69.

Cellulose carbon	34.33%
Distillate	43.32%
CO_2	5.22%
Other indifferent gases	17.13%

They calculate the distillate in percentage from the cellulose molecule as

Oxygen	8.50%
CO	54.14%
Residual gas	37.36%
Acetic acid	1.75%
Methyl alcohol	3.94%
Tar and other empyreumatic matters	9.70%

In contradistinction to the above results Klason was unable to even detect the presence of methyl alcohol, his results being confirmed by G. Büttner and H. Wislicenus.[1] Their figures calculated on 100% dry substance are as follows:

	1	2
Carbon	20.07%	30.56%
Tar	5.97%	7.10%
Acetic acid	2.76%	2.50%
Reducing substances	7.56%	6.91%
Ketones	0.04%	0.24%

The difference in the results of Experiments 1 and 2 are explained by the authors by the different manner of heating; in the first instance a gas stove was used, while in the second series of experiments an electric furnace was employed. Of the liquid products formed in the dry distillation of cotton cellulose, according to Cross and Bevan,[2] water, furfural, phenols, and liquid and solid hydrocarbons are contained in the tar. B. Tollens[3] adds allyl alcohol and creosote.

According to A. Scheurer[4] the exposure of cotton and dyes to sunlight and under a mercury quartz lamp with an exposure of 24 to 176 hours with cotton dyed a light shade with indigo, showed a series of color degradations. Prolonged exposure turned the samples yellow and an odor of ozone was perceptible.

---

[1] J. prakt. Chem. 1909, **79**, 177; abst. J. S. C. I. 1909, **28**, 417; Chem. Zentr. 1909, I, 1518; J. C. S. 1909, **96**, i, 290; Zts. ang. Chem. 1909, **22**, 1514; Chem. Ztg. Rep. 1909, **33**, 266; C. A. 1910, **4**, 1235; Jahr. Chem. 1909, II, 33; Meyer Jahr. Chem. 1909, **19**, 324.

[2] "Cellulose," page 69.

[3] "Cellulose" I, 233.

[4] Bull. Soc. Mulhouse, 1912, **80**, 324; abst. C. A. 1911, **5**, 1998; J. S. C. I. 1911, **30**, 279; Rev. gén. mat. col. 1910, **14**, 247; Rev. de Chim. 1911, **11**, 38; Meyer Jahr. Chem. 1910, **20**, 495.

Samples protected from the ozone by quartz plates faded more than samples in direct contact with the ozonized atmosphere, therefore the ozone did not produce the discoloration. Methylene blue dyed and Fehling's solution deposited cuprous oxide on the yellow portion, thus showing the presence of oxycellulose. A thin glass slide prevented the formation of the yellow color under it, while a quartz glass did not. The active rays of light are thus shown to have a wave length of between 3000 and 1860. The conclusion is drawn that ultra-violet rays act with much more energy upon benzo colors than upon indigo. Glass absorbs the ultra-violet rays which attack benzo colors. Color fading is not produced in every case by rays of the same wave length.

In an endeavor to gain an insight into the constitution of cellulose, E. Erdmann and C. Schaefer[1] examined the products of the dry distillation of filter paper, and found that when pure paper is heated in a copper retort until the volatile products are completely evolved, the condensed liquid products contain formaldehyde, furfural, maltol ($C_6H_6O_3$), oxymethylfurfurol and valerolactone. The gaseous products were found to consist mainly of carbon monoxide, methane and hydrogen.

The results of F. Fischer and H. Niggemann[2] on the influence of sodium hydroxide on the distillation of cellulose and wood is shown by the following table:

TABLE IV

	100 gm. of Cellulose	100 gm. of Cellulose with 100 cc. of $5N$ NaOH	100 gm. of Cellulose with 200 cc. of $5N$ NaOH	100 gm. of Cellulose with 200 cc. of $10N$ NaOH
Tar	5.5%	8.5%	15%	13%
Charcoal	20.0%	16.0%	15%	....
Gas	19 l.	36 l.	20 l.	39 l.

The addition of alkali caused an increase in the yield of gas and tar and a corresponding decrease in that of the charcoal residue. A similar influence was observed on sawdust, which yielded

---

[1] Ber. 1910, **43**, 2398; abst. J. Soc. Dyers Col. 1910, **26**, 252; abst. C. A. 1910, **4**, 3223; J. C. S. 1910, **98**, i, 718; J. S. C. I. 1910, **29**, 1198; Bull. Soc. Chim. 1911, (4), **10**, 445; Rep. de Chim. 1911, **11**, 117; Chem. Zentr. 1910, II, 1304; Jahr. Chem. 1910, II, 418; Meyer Jahr. Chem. 1910, **20**, 253.

[2] Abhand. Zur Kenntnis der Kohle, 1917, **1**, 176; Chem. Zentr. 1919, **90**, II, 521; J. S. C. I. 1919, **38**, 494-A.

16.5% of tar. The simultaneous introduction of steam or coal gas to accelerate the removal of distillation products diminished the yield of tar. An odor of peppermint, which was more marked on increasing the amount of alkali, was characteristic of these tars. They contain no paraffin hydrocarbons and are partly soluble in petroleum spirit. By the distillation of wood with zinc chloride, little tar and much charcoal are obtained, probably on account of the dehydrating action of the reagent.

Action of Light and Air upon Cellulose. The action of light and air upon cellulose has been studied but infrequently under conditions such as would exclude all outside influences. At a comparatively early time the action of sunlight and air upon such fabrics as curtains and their gradual change to a brown color and brittleness were noticed, but the simultaneous action of air (oxygen) and moisture is of considerable importance and has been observed in detail only but superficially. G. Witz[1] examined cellulose in the shape of old curtains which had been exposed to the sunlight for upwards of thirty years as well as other forms of cellulose which had been subjected to the influence of reflected light only. In both forms, apart from their brown color and brittleness, dyeing with basic dyestuffs as methylene blue, gave characteristic reactions for oxidized cellulose. In addition to the action of sunlight and air, it must be remembered that celluloses exposed for a considerable number of years as above, undoubtedly were under the influence of sulfurous and sulfuric acids from coal fire and perhaps gas light, and it is also possible, as first pointed out by A. Girard, that the textile may have included hydrocellulose formation which would at least partially explain the brittleness. Cellulose under diffused light and with moderate humidity, is but slowly affected in the open air.

Witz, in his endeavor to study the action of light with the exclusion of air and moisture, and especially with the exclusion of certain kinds of rays, placed the cotton under glasses which were painted over with some of the primary colors and in this condition the material was exposed during a whole summer to

[1] Bull. Soc. Rouen, 1883, **11**, 188; abst. J. S. C. I. 1883, **2**, 378; Jahr. Chem. 1883, 1782; Wag. Jahr. 1883, **29**, 1068; Tech. Chem. Jahr. 1884–5, 473; Faerb. Muster Ztg. **17**, 129. See also Bull. Soc. Rouen, 1882, 416; 1883, 169; abst. Dingl. Poly. 1883, **250**, 171, 172. D. R. P. 24173; abst. Wag. Jahr. 1883, **29**, 1068. E. P. 5914, 1882; abst. J. S. C. I. 1883, **2**, 412.

dry sunlight. As the result of his experiments, it was determined that oxycellulose was formed, especially under the influence of the blue rays, while the red and yellow rays were almost without any chemical influence whatsoever.

According to A. Girard[1] cotton is unaffected when left for months in a sealed tube containing oxygen. Metallic salts undoubtedly form a powerful catalyst for the action of light, air and moisture. Witz has been able to show that similar action occurs where dilute solutions of ammonium chloride, copper sulfate, or magnesium chloride, have been used in finishing fabrics and the fabrics thus treated exposed for a considerable time to light. In each instance it was demonstrated that oxycellulose had been formed as evidenced by the formation of a blue color with methylene blue and a yellow coloration on treatment with hot alkali. P. Jeanmaire[2] has demonstrated that cellulose also changes when iron oxides are formed within the fiber and has proven that when a fabric is saturated with (say) iron acetate, the tensile strength of the material is weakened in accordance with the strength of the solution and the temperature and duration of its action. This phenomenon cannot be attributable to the acid where acetic acid has been used, in contradistinction to the well-known action of the inorganic acids.

According to M. Prudhomme[3] oxidation occurs, which nor-

---

[1] Ann. Chim. Phys. 1881, (5), **24**, 337, 382; abst. Chem. News, 1881, **44**, 216; J. C. S. 1882, **42**, 378; Proc. U. S. Naval Inst. 1882, **8**, 309; Bull. soc. d'Encourage. **81**, 176; Bull. Musee, **82**, 80; Naturforscher, **15**, 26; Ber. 1881, **14**, II, 2834; Jahr. Chem. 1881, 985; Chem. Tech. Jahr. 1882–3, 508; Papier Ztg. 1882, 337. See also Ber. 1879, **12**, 2085, 2158; abst. Jahr. rein Chem. 1881, **9**, 460. Compt. rend. 1875, **81**, 1105; 1879, **88**, 1322; **89**, 165, 170; abst. Jahr. Chem. 1875, 786; 1879, 835, 1166; Jahr. rein Chem. 1875, 142.

[2] Bull. Soc. Mulhouse, 1889, **59**, 107; abst. Mon. Sci. 1889, **36**, 1447; Chem. Ztg. 1889, **13**, 1605; 1890, **14**, 186.

[3] Bull. Soc. Mulhouse, 1891, **61**, 509; Mon. Sci. 1891, **38**, 677; 1892, 495; abst. Chem. News, 1891, **64**, 9; J. C. S. 1891, **60**, 1447; J. S. C. I. 1891, **10**, 834; Bull. Soc. Chim. 1892, (3), **7**, 79; Compt. rend. 1891, **112**, 1374; Rev. gén. sci. 1891, **2**, 455; Ber. 1891, **24**, R, 595; Chem. Centr. 1891, II, 685; Chem. Tech. Rep. 1891, II, 123; Chem. Ztg. Rep. 1891, **15**, 1024; Jahr. Chem. 1891, II, 2816; Wag. Jahr. 1891, **37**, 1115; Zts. ang. Chem. 1892, **5**, 718; Tech. Chem. Jahr. 1891–2, **14**, 491; Industrieblatter von Jacobsen, 1892, 262; Deut. Chem. Ztg. 1891, 218. See also H. Koechlin, Bull. soc. ind. Rouen, 1889, 332; Bull. Soc. Mulhouse, 1889, Sept. Appendix, 39; Chem. Tech. Rep. 1889, I, 83; Tech. Chem. Jahr. 1889–90, **12**, 494; J. S. C. I. 1890, **9**, 387; Mon. Sci. 1889, 745. H. Koechlin-Baumgartner, Faerb. Muster. Ztg. 1890, No. 23; Bayer Ind. Gew. **22**, 441; Jahr. Chem. 1890, 2886; Chem. Tech. Rep. 1890, II, 55.

mal oxidizing action of the air is accelerated, presumably catalytically, by the presence of the iron oxides.

There is little doubt but what the so-called yellowing of cellulose as observed in old papers and fabrics, is due primarily to the combined action of light and air and the action of catalysts. These catalysts are metallic salts, iron resinates and the ammonia residues from the bleaching process.

The action of radium[1]—probably owing to the oxidation of the oxygen of the air—considerably weakens cotton fiber. Double refraction in some fibers has been used as a means for distinguishing certain kinds of filaments. Cotton cellulose observed with crossed nicols appears almost colorless or only slightly greyish, while linen and ramie show a vivid play of colors.[2] According to Behrens and Herzog, the flat cotton fiber seen in the direct light of the narrow side (edge) appears distinctly green.

A. Pauly[3] maintains that the double refraction permits a conclusion to be reached as to the tensile strength of the fiber.

According to N. Gaidukow[4] the ultramicroscope permits the ready differentiation of cotton from other fibers and is destined to become a valuable auxiliary for the examination of textile fibers.

J. Schneider and G. Kunzl[5] have also made ultramicroscopic observations of cotton filaments.

Absorption of Tannins by Cellulose. A powerful affinity for cellulose is exerted by gallotannic acid and the tannins in general, advantage being taken of this property in the use of the tannins as mordants in dyeing. In this respect, tannic acid is unlike other acids, cotton being capable of absorbing up to 10%

---

1. Selleger, Papier-Fabrikant, 1907, **6,** 1349, 2083. See also E. Selleger, Papier-Fabrikant, 1906, **4,** 2213; abst. Zts. ang. Chem. 1907, **20,** 452. Kollman, Papier Ztg. 1906, 3061; abst. Zts. ang. Chem. 1907, **20,** 452.

For data on the exposure of cotton cellulose under mercury quartz lamp, see A. Scheurer, Bull. Soc. Ind. Mulhouse, 1910, **80,** 324; abst. C. A. 1911, **5,** 1998; J. S. C. I. 1911, **30,** 729; Rev. gén. mat. col. 1910, **14,** 247; Rept. Chim. 1911, **11,** 38; Meyer Jahr. Chem. 1910, **20,** 495.

2. Herzog, Zts. Farb. Ind. 1908, **7,** 183, 218, 204, 216; abst. Chem. Zentr. 1908, II, 547; Meyer Jahr. Chem. 1908, **18,** 501; Zts. ang. Chem. 1908, **21,** 2557; Chem. Ztg. Rep. 1908, **32,** 436.

3. Zentr. Oesterr. ungar. Papier Ind. 1907, 321; abst. Chem. Ztg. Repert. 1907, **31,** 245.

4. Zts. Farb. Ind. 1908, **7,** 251, 267; abst. Chem. Zentr. 1908, I, 1217; 1908, II, 1068; Färber. Ztg. 1907, **18,** 392; C. A. 1908, **2,** 3151; Jahr. Chem. 1905-8, II, 3181; Zts. ang. Chem. 1908, **21,** 393.

5. Zts. wiss. Mikr. 1908, **23,** 393; abst. Chem. Zentr. 1908, I, 308.

of its weight of tannic acid from an aqueous solution. According to W. Gardner and T. Carter,[1] cotton cellulose possesses the power of absorbing from 30% to 32% of gallotannic acid but no gallic acid. In the presence of a relatively small proportion of a lower fatty acid, such as formic or acetic acid, the amount absorbed is increased to 48–50%. They found, for instance, that a solution of one gram per liter of tannin was absorbed in 3 hours by cellulose, as follows:

Acetic Acid per Liter	Tannin Absorbed
0	30–32%
1	35–36%
2	40–42%
5	49–51%
10	32–34%
20	31–32%

Little or no difference was found if formic or propionic acid was used in equivalent amount instead of acetic acid, or polybasic organic acids, as the following results show:

	Quantity Absorbed in Per cent.
Tannin	32
Tannin and acetic acid	48–50
Tannin and citric acid	19–21
Tannin and tartaric acid	20–22
Tannin and sulfuric acid	18–20
Tannin and hydrochloric acid	30–32
Tannin and sodium acetate	16–18

Dreaper and Wilson have extended this investigation to also include the action of salts.

Other hydroxyl-containing substances show, under certain conditions, an entirely different behavior from tannin,[2] phenol being retained. For instance, from 0.1% solutions, 10 gm. cotton absorbed the following per cent.:

---

[1] J. Soc. Dyers Col. 1898, **14,** 143; abst. J. S. C. I. 1898, **17,** 843; Rev. mat. color. 1898, **2,** 316; Meyer Jahr. Chem. 1899, **9,** 446.

[2] Mansier, Jour. Pharm. chim. 1902, **16,** 60, 116; abst. J. C. S. 1902, **82,** ii, 690; J. S. C. I. 1902, **21,** 1098, 1155; Rep. Chim. 1902, **2,** 524; Chem. Centr. 1902, II, 768, 769; Jahr. Chem. 1902, 238.

Tannic acid	32
Catechutannic acid	32
Gallic acid	0.0
Pyrogallol	4.5
Phloroglucin	24–26
Protocatechuic acid	0.0
Pyrocatechin	0.0
Resorcin	45–50
Salicylic acid	0.0
Guaiacol	0.0

From the above results it would appear that the property of absorption is a function of the meta position. An explanation based merely upon capillary effect is untenable, and the instability speaks against a chemical union, because the adsorbed material is removable by washing with cold water. F. Kraft[1] has sought an explanation based on an assumed colloidal character for tannic acid. If a chemical combination does exist between the cellulose and the tannin, it must be of a very loose description. Cotton exhibits the same attraction for tungstic acid and some of the uranium salts, but the expense of the latter preclude their commercial application at the present time as mordanting agents.

Other investigations of the absorptive capacity of cellulose for tannin have been made by C. Koechlin,[2] G. Georgievics,[3] W. Dreaper and A. Wilson,[4] F. Blockey,[5] and E. Knecht and J. Kershaw.[6]

Cellulose and Dyestuffs. Persoz, as far back as 1846,[7] drew attention to the fact that cotton absorbs aluminum from an

---

[1] Ber. 1899, **32**, 1618; abst. J. C. S. 1899, **76**, ii, 472; J. S. C. I. 1899, **18**, 757; Bull. Soc. Chim. 1900, **24**, 399; Rev. Chim. 1899, **1**, 487; Chem. Centr. 1899, II, 169; Chem. Tech. Rep. 1899, 371; Chem. Ztg. Rep. 1899, **23**, 199; Jahr. Chem. 1899, 110; Meyer Jahr. Chem. 1899, **9**, 448.

[2] Bull. Soc. Mulhouse, 1884, **51**, 438; abst. J. C. S. 1885, **48**, 208; J. S. C. I. 1889, **8**, 342; Dingl. Poly. 1884, **253**, 86; Jahr. Chem. 1884, 1851; Wag. Jahr. 1884, **30**, 1138.

[3] Gewerbemuseum, 1898, **8**, 362; Färb. Ztg. 1891–1892, **3**, 402; abst. J. S. C. I. 1898, **17**, 845; Chem. Centr. 1899, I, 313; Chem. Tech. Rep. 1899, 402; Chem. Ztg. Rep. 1898, **22**, 242; Jahr. Chem. 1899, 105; Meyer Jahr. Chem. 1898, **8**, 490.

[4] Proc. Chem. Soc. 1906, **22**, 70; J. S. C. I. 1906, **25**, 515; Mon. Sci. 1907, **66**, 280; abst. Bull. Soc. Chim. 1907, (4), **2**, 63; Rep. Chim. 1906, **6**, 347; Chem. Centr. 1906, I, 1621; Chem. Ztg. 1906, **30**, 253.

[5] Collegium, 1903, **2**, 76; J. S. C. I. 1903, **22**, 763; abst. Chem. Ztg. Rep. 1903, **27**, 144.

[6] Jour. Soc. Dyers Col. 1892, **8**, 45; Faerb. Ztg. 1891–1892, **3**, 402; J. S. C. I. 1892, **11**, 129; Chem. Centr. 1892, I, 686; Chem. Tech. Rep. 1892, I, 62; Chem. Ztg. Rep. 1892, **16**, 116; Jahr. Chem. 1892, 2907; Meyer Jahr. Chem. 1892, **2**, 509; Wag. Jahr. 1892, **38**, 978.

[7] "Traite de l'impression," 1846, **2**, 138.

aluminum acetate solution, especially when the aluminum is in a state of colloidal solution as aluminum acetate.[1] The investigations of the action of mordants on cellulose by W. Saposchnikoff and W. Minajeff[2] have, in the main been contradictory, although the latter[3] has shown that the wall of cotton cells vary greatly in their permeability to mordant solutions. Bowman[4] established the fixation of aluminum oxide from alum solutions and has shown that the crystalloid portion of the alum diffuses through the exterior membrane of the cotton fiber, which therefore acts as a dialyzing membrane while the colloidal portion is retained by the membrane in the insoluble state. M. Fluri[5] and Runge[6] have also investigated this phenomena, but not with concordant results.

P. Zacharias,[7] C. Liebermann,[8] W. Biltz,[9] W. Suida[10] and L.

---

1. Pharm. Zentralhalle, 1909, **50**, 395; abst. Chem. Ztg. Rep. 1909, **33**, 345; C. A. 1910, **3**, 1910; Chem. Zentr. 1909, II, 142.
2. Zts. Farbenind. 1903, **2**, 259; 1904, **3**, 164; 1905, **4**, 81; abst. J. S. C. I. 1903, **22**, 903; 1904, **23**, 604; 1905, **24**, 272; Rep. Chim. 1903, **3**, 380; Chem. Centr. 1903, II, 471; 1904, I, 1584; 1905, I, 906; Jahr. Chem. 1903, 1560; 1904, 1811; 1905–1908, II, 3174; Wag. Jahr. 1903, II, 523; Zts. ang. Chem. 1905, **18**, 585; Meyer Jahr. Chem. 1905, **15**, 510.
3. Zts. Farbenind. 1907, **6**, 236, 252, 309, 345; abst. J. S. C. I. 1907, **26**, 1236; Chem. Zentr. 1908, I, 308; Jahr. Chem. 1905–1908, II, 3175; Zts. ang. Chem. 1908, **21**, 1255.
4. "The Structure of Cotton Fibre," page 435.
5. Flora, 1908, **99**, 81; Naturw. Rundsch. 1909, **23**, 610; abst. Bied. Zentr. 1909, **38**, 670; C. A. 1908, **2**; 3370; J. C. S. 1909, **96**, ii, 338, 1046; Chem. Zentr. 1909, I, 386; Chem. Ztg. Rep. 1908, **32**, 547.
6. "Farbenchemie, Die Kunst zu drucken," 1842, **2**, 1.
7. "Die Theorie der Faerbevorgaenge," 1908.
8. Ber. 1893, **32**, 1574; abst. J. C. S. 1893, **64**, i, 513; J. S. C. I. 1894, **13**, 28; Bull. Soc. Chim. 1893, **10**, 1083; Chem. Centr. 1893, II, 342; Jahr. Chem. 1893, 610; Meyer Jahr. Chem. 1893, **3**, 521; Wag. Jahr. 1893, **39**, 1005.
9. Nachr. Gess. Wissensch. Göttingen, 1904, 1; Ber. 1904, **37**, 1766; abst. J. C. S. 1904, **86**, ii, 392; J. S. C. I. 1904, **23**, 439; Bull. Soc. Chim. 1905, **34**, 176; Rep. Chim. 1905, **5**, 111; Chem. Centr. 1904, I, 1039; Chem. Ztg. Rep. 1904, **28**, 175; Chem. Zts. 1904, **3**, 783; Jahr. Chem. 1904, 99, 1804; Zts. ang. Chem. 1904, **17**, 1833; 1905, **18**, 585; Nachr. Gess. Wissensch. Göttingen, 1905, 46; Ber. 1905, **38**, 184, 2963, 4143; abst. J. C. S. 1905, **88**, i, 224; Bull. Soc. Chim. 1906, **36**, 436; Rep. Chim. 1906, **6**, 158; Chem. Centr. 1905, I, 475; II, 524; Chem. Ztg. Rep. 1905, **29**, 363; Jahr. Chem. 1905–1908, II, 3151; Zts. ang. Chem. 1906, **19**, 1473. See also P. Zacharias, Ber. 1904, **37**, 4387; 1905, **38**, 816; Fifth Intern. Cong. Chem. 1903, II, 94; abst. J. C. S. 1905, **88**, i, 74, 293; Bull. Soc. Chim. 1905, **34**, 629, 786; Rep. Chim. 1905, **5**, 111; Chem. Centr. 1905, I, 127, 906; Jahr. Chem. 1904, 99, 1804; 1905–1908, II, 3151, 3153; Meyer Jahr. Chem. 1905, **15**, 519; see also Färberztg. 1901, 149, 165; Zts. physik. Chem. 1902, **39**, 468; Chem. Ztg. 1902, **26**, 290; Zts. Farben u. Textil-Chem. 1903, **2**, 233.
10. Monatsh. 1904, **25**, 1107; 1905, **26**, 413; Wien. Akad. Ber. **113**, 725; abst. J. C. S. 1905, **88**, i, 75; J. S. C. I. 1904, **23**, 1144; Bull. Soc. Chim.

Liechti and W. Suida[1] have attempted analyses of alizarin lakes, but their results are inconclusive.[2] F. Krafft[3] and W. Crum,[4] as well as the later work of W. Minajeff,[5] have shown as the result of examination of microscopical photographs that the fiber is mostly dyed superficially. F. Krafft[6] was the first to point out the colloidal nature of tannic acid when employed with tartar emetic as the foundation for the application of basic dyestuffs. F. Erban,[7] L. Vignon[8] and Persoz[9] have shown that insoluble lead salts like those that are soluble, are retained by the fiber, especially if the cotton be subsequently passed through a solution of the calcium salt. According to W. Elbers[10] and Lauber,[11]

1905, **34**, 437; Rep. Chim. 1905, **5**, 484; Chem. Centr. 1905, I, 128, 974; Chem. Ztg. 1904, **28**, 626; Jahr. Chem. 1904, 185; Meyer Jahr. Chem. 1905, **15**, 512; Tschermak's Mitt. 1905, **23**, 534.

[1] Mitt. Gewerbemus. 1885, Nos. 1, 2, 3, 4; 1886, **3**, 1; abst. J. S. C. I. 1886, **5**, 523; Mon. Sci. 1887, **29**, 270; Chem. Ztg. Rep. 1886, **10**, 11; Jahr. Chem. 1886, 2206; Wag. Jahr. 1886, **32**, 919; Chem. Tech. Jahr. 1885–1886, **8**, 426.

[2] W. Biltz has investigated this point for the system alizarin in alkaline solution against ferric oxide and the relation of the composition of the dye-lakes formed to the concentration of its components. In this case the existence of a chemical compound was proven, but the behavior of alizarin red SW towards chromic oxide was found to indicate the formation of an absorption compound.

[3] Ber. 1899, **32**, 1618; abst. J. C. S. 1899, **76**, ii, 472; Chem. Centr. 1899, II, 169; J. S. C. I. 1899, **18**, 757; Jahr. Chem. 1899, 110; Bull. Soc. Chim. 1900, **24**, 399; Rev. Chim. 1899, **1**, 487; Chem. Ztg. Rep. 1899, **23**, 199.

[4] Bull. Mulhouse, 1864, **34**, 385; J. C. S. 1863, **16**, i, 404; abst. Chem. Centr. 1863, 927; 1864, 238; abst. Jahr. Chem. 1863, **16**, 782; Wag. Jahr. 1863, **9**, 615.

[5] Zts. Farbenind. 1905, **4**, 81; 1907, **6**, 234; 1908, **7**, 345; 1909, **8**, 313; abst. J. S. C. I. 1907, **26**, 1236; Chem. Centr. 1905, I, 906; 1908, I, 308; Wag. Jahr. 1908, II, 458; Zts. ang. Chem. 1908, **21**, 1255.

[9] Ber. 1893, **32**, 1618; abst. J. C. S. 1899, **76**, ii, 472; J. S. C. I. 1899, **18**, 751; Bull. Soc. Chim. 1900, **24**, 399; Rev. Chim. 1899, **1**, 487; Chem. Centr. 1899, II, 169; Chem. Ztg. Rep. 1899, **23**, 199; Jahr. Chem. 1899, 110.

[7] Zts. für Textil Ind. 1909, **13**, 117; Färberztg. 1909, **20**, 5, 24; abst. Chem. Zentr. 1909, I, 598; Chem. Ztg. Rep. 1909, **33**, 152; Wag. Jahr. 1909, II, 493.

[8] Rev. mat. Col. 1909, **13**, 316; Bull. Soc. Mulhouse, **79**, 244; abst. C. A. 1910, **4**, 386; J. C. S. 1909, **96**, ii, 576; J. S. C. I. 1909, **28**, 651; Bull. Soc. Chim. 1909, (4), **5**, 675; Compt. rend. 1909, **148**, 1329; Rep. Chim. 1909, **9**, 464; Chem. Zentr. 1909, II, 156; Chem. Ztg. 1909, **33**, 720; Chem. Ztg. Rep. 1909, **33**, 424; Jahr. Chem. 1909, I, 875, 876.

[9] "Traite de l'impression," **2**, 126.

[10] D. R. P. 101190, abst. Mon. Sci. 1899, **54**, 79; Chem. Centr. 1899, I, 1092; 1900, I, 699; Chem. Tech. Rep. 1899, 53; Chem. Ztg. 1899, **23**, 152; Jahr. Chem. 1899, 2205; Wag. Jahr. 1899, **45**, 1062; Zts. ang. Chem. 1899, **12**, 231. D. R. P. 106708; abst. Chem. Centr. 1900, I, 699; Wag. Jahr. 1899, **45**, 960. E. P. 509, 1898; abst. J. S. C. I. 1899, **18**, 39. E. P. 6546, 1898; abst. J. S. C. I. 1899, **18**, 39. F. P. 274053; abst. Mon. Sci. 1899, **54**, 42. F. P. 278376. Russ. P. 2664, 1899.

[11] "Handbuch des Zeugdrucks," 1902, 2nd Ed., **2**, 228.

when indigo paste is applied to cellulose in the fabric the indigo sublimates into the interstices of the fiber. W. Minajeff[1] has partially established the fact that the amount of dyestuff absorbed is directly proportional to the concentration, no physical absorption in general occurring, although apparently a certain amount of absorption occurs in soaking the fiber with *b*-naphthol and naphthylamin solutions. E. Justin-Mueller[2] and C. Schwalbe and W. Hiemenz[3] have shown that in dyeing produced with azo colors developed in the fiber the addition of oil or sulfonated oil plays an important part in the percentage of dyestuff absorption. R. Haller,[4] C. Liebermann,[5] H. Freundlich and G. Losev,[6] G. von Georgievic and L. Loewy[7] and G. von Georgievic,[8] together with C. Weber[9] and W. Suida and P. Gelmo[10] have made exhaustive investigations.[11]

Cellulose Solvents. No simple solvent for so-called normal cellulose, of which cotton is the type, is at present known. By

---

[1] Zts. Farbenind. 1905, **4**, 81; 1907, **6**, 234, 252, 309, 451; 1908, **7**, 345; 1909, **8**, 313; abst. J. S. C. I. 1907, **26**, 1236; Chem. Centr. 1905, I, 906; Chem. Zentr. 1908, I, 308; Wag. Jahr. 1908, II, 458; Zts. ang. Chem. 1908, **21**, 1255.

[2] 6th Intl. Cong. Appl. Chem; abst. Zts. Farbenind. 1906, **5**, 272; Chem. Centr. 1906, II, 640; J. S. C. I. 1906, **25**, 532; Zts. ang. Chem. 1906, **19**, 852.

[3] Zts. Farbenind. 1906, **5**, 109; abst. Chem. Centr. 1906, I, 1469.

[4] Zts. Farbenind. 1907, **6**, 126; J. S. C. I. 1907, **26**, 523.

[5] Dingl. Poly. 1866, **181**, 133; abst. Jahr. Chem. 1866, 895; Zts. anal. Chem. 1866, **5**, 463; Vierteljahrsschr. pr. Pharm. **16**, 446; Bull. Soc. Chim. 1866, **6**, 506.

[6] Zts. phys. Chem. 1907, **59**, 284; abst. J. S. C. I. 1907, **26**, 682; Chem. Zentr. 1907, II, 274; J. C. S. 1907, **92**, ii, 534; Biochem. Centr. 1907, **6**, 373; Chem. Ztg. Repert. 1907, **31**, 283; C. A. 1907, **1**, 2343.

[7] Monatsh. 1895, **16**, 345; abst. J. C. S. 1895, **68**, i, 668; Jahr. Chem. 1895, 196.

[8] Monatsh. 1894, **15**, 705; abst. J. C. S. 1895, **68**, ii, 259.

[9] Faerber Ztg. 1893, **22**, 185.

[10] Monatsh. 1906, **27**, 225, 1193; Zts. Farbenind. 1907, **6**, 41; Wien. Akad. Ber. **115**, IIb, 997; abst. C. A. 1907, **1**, 1174; J. C. S. 1906, **90**, i, 445; 1907, **92**, i, 231; J. S. C. I. 1907, **26**, 89; Chem. Zentr. 1907, I, 853; Jahr. Chem. 1905–1908, II, 3161, 3162; Zts. ang. Chem. 1907, **20**, 771, 773.

[11] Behrens, Chem. Ztg. 1903, **27**, 1252. Biltz, Ber. 1905, **38**, 2963; 1907, **38**, 2973. Dreaper, J. S. C. I. 1894, **13**, 96; Rev. Mat. Col. 1905, **9**, 133. Erdmann, Chem. Ind. 1896, **19**, 6. H. Freundlich, Zts. physik. Chem. 1906, **57**, 385. H. Freundlich and G. Losev, Zts. physik. Chem. 1907, **59**, 284. G. von Georgievics, Chem. Ztg. 1902, **26**, 129. G. von Georgievics and Loewy, Monatsh. 1894, **15**, 705; 1895, **16**, 345. Gnehm and Kaufler, Zts. ang. Chem. 1902, **15**, 345. Gnehm and Roetheli, Zts. ang. Chem. 1898, **11**, 482, 501. Haller, Zts. Farben Textil Chem. 1907, **6**, 128. Heidenhaim, Pfluegers Archiv. 1903, **100**, 217; Chem. Centr. 1904, I, 116. Herrmann, Färber. Ztg. 1904, **15**, 218. Huebner, J. C. S. 1907, **91**, 1059, 1064, 1068, 1071. Justin-Mueller, Zts. Farben. Textil Chem. 1903, **2**, 365; 1904, **3**, 251;

solvent of a substance is understood that liquid which has a dissolving influence and at the same time permits the recovery of the cellulose from the solvent without change in its material properties, especially its chemical deportment. All cellulose compounds going into solution are precipitated in modified forms and the esters prepared from these forms appear to be not derivatives of normal cellulose, but of a form of hydrocellulose whose nature has, up to the present, not been definitely determined. The so-called solutions of cellulose are really colloidal solutions. The reagents which have a dissolving influence upon cellulose may be classified as follows:

1. Concentrated solution of zinc salts upon heating, or in conjunction with mineral acids as hydrochloric acid. Zinc chloride, zinc bromide, zinc iodide and zinc chlorate have been patented for this purpose.

2. Ammoniacal solutions of copper salts, as the hydroxide, carbonate and chloride, and solutions of copper hydroxide in alkylamines.

3. Powerful mineral acids as sulfuric, hydrochloric, phosphoric and nitric (sp. gr. 1.52) are known to dissolve cellulose, especially when the acid is in a concentrated form. Concentrated solutions of mercuric chloride, bismuth chloride, stannous chloride, antimony pentachloride, stannic chloride and titanium tetrachloride mixed with varying amounts of hydrochloric acid. In the latter case one can best observe the dissolving effect from the fact that the cellulose fibers swell up and become translucent before passing into solution.

4. Certain organic reaction mixtures in which the cellulose

Rev. Mat. Col. 1909, **13**, 75; Zts. Farben.-Ind. 1909, **8**, 93; Zts. Chem. Ind. Kolloide. 1909, **5**, 235. Kaufler, Zts. physik. Chem. 1903, **43**, 686. Knecht, Färber. Ztg. 1899, **10**, 60; J. Soc. Dyers Col. 1909, **25**, 194. Krafft, Ber. 1889, **32**, 1618. R. Meyer and J. Maier, Ber. 1903, **36**, 2972. R. Meyer and J. Schaefer, Ber. 1894, **27**, 3355. Michaelis, Pfluegers. Archiv. 1903, **97**, 634; Chem. Centr. 1903, II, 608; Beitraege, Z. Chem. Physiol. and Patholgie, 1906, **8**, 46. Minajeff, Zts. Farben.-Ind. 1907, **6**, 312. de Mosenthal, J. S. C. I. 1904, **23**, 293. Pelet-Jolivet, Bull. Mulhouse, 1909, **79**, 155; Zts. Chem. and Ind. der Kolloide, 1908, **3**, 275; 1909, **5**, 238. Roetheli, Dissertation, Zurich, 1898, 58. Rosenstiehl, Compt. rend. 1909, **149**, 396; Chem. Centr. 1909, II, 1504. Schmidt, Zts. Phys. Chem. 1894, **15**, 60. Suida and Hoehnel, Färber. Ztg. 1905, **5**, 105. Teague and Buxton, Zts. physik. Chem. 1907, **60**, 484. Vignon, Rev. Mat. Col. 1897, **1**, 221; 1909, **13**, 185. Weber, Färber. Ztg. 1893, **4**, 186, 201, 202, 213. P. Wilhelm, Zts. Farben. Textil Chem. 1901, **4**, 1901. Witt, Färber. Ztg. 1890, **1**, 1. Zacharias, Färber. Ztg. 1901, **12**, 149. Zts. Farben. Textil. Ind. 1895, **4**, 465.

dissolves with the production of esters as in the formylation and acetation of cellulose, and in the preparation of cellulose ethers, as by ethylation. In all of the above instances the cellulose may be quantitatively recovered from this solution although constitutionally altered. A so-called solution of cellulose in water may be effected by the combined action of alkali and carbon bisulfide. Neither carbon bisulfide nor alkali, however, can be properly designated as solvents. The xanthates of cellulose (viscose) belong to this category. According to P. Weimarn[1] cellulose may be dissolved in solutions of most salts when heated under pressure.

In addition to this observation of P. Weimarn, others have recorded that upon heating concentrated solutions of metallic salts such as zinc or magnesium chlorides with cellulose, the latter is converted either into a plastic material or passes entirely into solution. For instance, J. Huebner and W. Pope[2] have pointed out that a saturated solution of potassium iodide or other iodides can initiate a similar change under the action of heat or pressure, alone or together. A saturated aqueous barium-magnesium iodide solution has a similar effect. A. Scheurer[3] records that when cellulose is heated to 140° with zinc chloride, or with tin chloride of 5° Bé., the cellulose undergoes material change. With stoicheiometrical quantities of calcium or/and magnesium chloride there is but slight action, while with sodium or potassium chlorides, potassium iodide, ammonium chloride or barium chloride, operating under similar conditions, but little or no change appears to occur.

Action of Cuprammonium Solutions on Cellulose. A "solvent" of cellulose of a wide range of application, and of great commercial importance in that an industry of artificial silk manufac-

---

[1] Koll. Zts. 1912, **11**, 41; abst. Chem. Zentr. 1912, II, 817; C. A. 1912, **6**, 3516; J. C. S. 1912, **102**, i, 679; J. S. C. I. 1912, **31**, 768. As far back as 1858, A. Vogel (Ber. Münchener Acad; abst. Instit. 1858, 151; Jahr. Chem. 1858, 481) observed that lead acetate solution dissolved filter paper.

[2] J. S. C. I. 1904, **23**, 404; abst. Zts. Farben u. Textil. Chem. **2**, 315; Chem. Centr. 1904, I, 1625; Chem. Zts. 1903-1904, **3**, 77; Jahr. Chem. 1904, 1813; Zts. ang. Chem. 1904, **17**, 777. (This article is accompanied by colored microphotographs of cotton fiber under polarized light.) See J. Barral and Salvetat, Ann. Chim. Phys. 1876, (5), **9**, 126; Compt. rend. 1875, **81**, 1189; Chem. News, 1876, **33**, 18; J. C. S. 1876, **29**, 821; Bull. Soc. Chim. 1876, **25**, 425; Ber. 1876, **9**, 68; Mon. Sci. 1876, **18**, 90; Dingl. Poly. 1876, **219**, 469; Jahr. Chem. 1875, 1164.

[3] Bull. Soc. Mulhouse, 1883, **53**, 76; abst. Wag. Jahr. 1883, **29**, 1053.

ture has been founded upon the principles involved, is cuprammonium solution. It is said that the solvent action of such a solution was first observed by E. Schweizer[1] in 1857, and "Schweizer's Solution" (usually incorrectly spelled Schweitzer) from that time to the present is the name that has been applied to cuprammonium solutions. This discovery has also been attributed to Mercer, who employed a solution of ammonia of 0.92 specific gravity, which was saturated with cupric hydroxide at ordinary temperatures and then diluted with three volumes of water. Mercer investigated closely the various phases of this reaction in respect to the influence of the conditions of concentration and treatment, and demonstrated that speed of solution was retarded by the presence of salts, and that therefore the solutions obtained by decomposing copper salts with an excess of ammonia were much less reactive than equivalent amounts of the pure hydroxide.

He also showed that the reactivity was materially decreased by elevating the temperature, and that concordant solutions of maximum stability were only producable when the temperature was low and kept under strict control. He devised an interesting method of demonstrating the solvent capacity for the cuprammonium solutions upon cellulose, by applying a solution of cupric nitrate to cotton cloth—preferably previously mercerized—then immersing the cloth into a dilute solution of caustic soda. After washing to remove the major portion of the alkali and partially drying, the cloth was exposed to the action of gaseous ammonia, when the treated portions of the fabric would gelatinize and eventually pass into solution, leaving the untreated portion sub-

---

[1] J. prakt. Chem. 1857, **72**, 109, 344; Zts. Pharm. 1859, 110; Poly. Notiz. 1859, 157; Dingl. Poly. 1859, **152**, 302; Bayer. Kunst. u. Gewerbebl. 1859, 372; Chem. Tech. Mitth. 1858–1859, 77. Compare J. Schlossberber, J. prakt. chem. 1858, **73**, 373; Vierteljahrsschrift der naturforschenden Gesellschaft in Zurich, 1857, **2**, 396. See Dingl. Poly. 1874, **213**, 361; Chem. Tech. Mitth. 1874–1875, 196. Cramer (J. prakt. Chem. 1858, **73**, 1) came to the conclusion from osmotic measurements, that ammoniacal copper dissolved cellulose to a true solution, while Erdmann considered it to be a very highly hydrated gel. Cross and Bevan (Textbook of Paper Making, 8) have expressed the view that the copper compound combines with the cellulose to form a colloid double salt. H. Baubigny, Compt. rend. 1887, **104**, 1616. Neubauer, Zts. anal. Chem. 1875, **14**, 196; abst. Poly Notiz. 1875, 255; Chem. Tech. Mitth. 1875–1876, 141. E. Mulder, Scheik. Onderz, **3**, 156; Jahr. Chem. 1863, **16**, 566. M. Rosenfeld, Ber. 1879, **12**, 956. Compare Bronnert, Fremery and Urban, D. R. P. 119230.

stantially unacted upon, although continued action had an effect.

The preparation of the cuprammonium solution which is to be used for dissolving the cellulose is of considerable technical importance, and involves close attention to many seemingly unimportant details, especially when the solution is to be used for artificial filament formation. The solutions of the cuprammonium compounds in general attack normal cellulose but slowly, unless the cellulose has been hydrolyzed by previous treatment with caustic soda solution but with excess of ammonia solution proceeds energetically, gelatinous hydrates being first formed, which finally entirely pass into solution. It appears that solutions of pure cuprammonium hydroxide exert a greater dissolving power than do those solutions resulting from the decomposition of a copper salt with excess of ammonia. The two methods in general use at the present time for producing cuprammonium solutions are as follows:

1. To an aqueous solution of a cupric salt is added ammonium chloride, and then sufficient sodium hydroxide to produce the maximum of blue precipitate. This latter is thoroughly washed with cold or warm water upon a cloth filter, centrifugalized, and immediately dissolved in the cold in the minimum amount of ammonia. Before use it is carefully filtered and kept at a low temperature until required.

2. In the second method copper, either in thin sheets or copper shavings or turnings, is placed in a glass receptacle and covered with ammonia of 0.92 gravity. Atmospheric air is aspirated through the container at such speed as to amount to about 40 times the volume of liquid used per hour. After six to eight hours substantial solution takes place, the liquid having the composition of ammonia 10–15%, copper (calculated as CuO) 2.0%–2.5%. In the C. Wright method,[1] a solution of cuprammonium hydroxide is obtained by piling pieces of copper loosely in vertical iron towers, preferably arranged in series, down which water is caused to trickle, while air mixed with ammonia is admitted from below. A weak solution of ammonia or of cuprammonium hy-

---

[1] E. P. 737, 1883. J. S. C. I. 1884, **3**, 121; Mon. Sci. 1884, **26**, 1134. J. Scoffern (U. S. P. 86103). waterproofed paper and woven fabrics with "copperized ammonia," as far back as 1869. See E. Grimaux, Compt. rend. 1884, **98**, 1434. Maumené, Compt. rend. 1882, **95**, 223. G. Bradbook, U. S. P. 1244463, 1919, describes a cuprammonium and casein adhesive.

droxide may be used instead of water. The air and ammonia are led successively through the connected towers, and the weak solutions thus obtained are systematically used instead of water. The proportion of copper in the solution may be increased by immersing copper in it and blowing air through the solution, or the solution may be run down a tower packed with copper, air meanwhile being forced upwards. To obtain solutions containing zinc-ammonium hydroxide, with or without the cuprammonium compound, fragments of brass or other copper-zinc alloy is used in the process instead of copper.

M. Prud'homme[1] prefers to use potassium instead of sodium hydroxide. H. Pauly proposed to accelerate the solvent action by means of the presence of scraps of platinum or by means of an electric current.[2] Titanous and chromous salts[3] have been suggested for the same purpose. According to B. Borzykowski[4] an ammoniacal copper solution containing a maximum of copper and a corresponding minimum of ammonia is produced by adding, to an ordinary ammoniacal copper solution, aqueous solutions of copper sulfate and caustic alkali, whereby the cupric hydroxide dissolves as soon as formed.

In another method,[5] the solvent for cellulose is prepared by

---

[1] F. P. 344138, 1904; abst. J. S. C. I. 1904, **23**, 1087; Mon. Sci. 1906, **65**, 34.

[2] E. P. 28631, 1897. F. P. 272718; abst. Mon. Sci. 1898, **52**, 200. D. R. P. 98642, 1897; abst. Jahr. Chem. 1898, 1370; Wag. Jahr. 1898, **44**, 994; Chem. Centr. 1898, II, 911. Belg. P. 132273, 1897. In this connection see: A. Healy, E. P. 174, 1878. M. Neumann, U. S. P. 241056, 1881. W. Beddinghaus, E. P. 20359, 1894; abst. J. Soc. Dyers Col. 1896, **12**, 25.

[3] P. Spence & Sons, F. P. 449801, 1912; abst. C. A. 1913, **7**, 3025; J. S. C. I. 1913, **32**, 483. E. P. 25532, 1911; abst. J. S. C. I. 1913, **32**, 18. D. R. P. 264952, 1912; abst. C. A. 1914, **8**, 248. F. P. 449803, 1912; abst. J. S. C. I. 1913, **32**, 483; C. A. 1913, **7**, 3025. E. P. 25333, 1911; abst. J. S. C. I. 1913, **32**, 18. D. R. P. 264951, 1912; abst. C. A. 1914, **8**, 248. D. R. P. Anm. S-37390, 37391, 37392; abst. Kunst. 1913, **3**, 200. Belg. P. 250442, 1912; abst. Kunst. 1913, **3**, 235. Belg. P. 250441, 1912.

[4] U. S. P. 1100518; 1914; J. S. C. I. 1914, **33**, 746. E. P. 24996, 1912; J. S. C. I. 1913, **32**, 283; Jour. Soc. Dyers Col. 1913, **29**, 171; C. A. 1913, **7**, 3025. F. P. 450193, 1912; J. S. C. I. 1913, **32**, 483; C. A. 1913, **7**, 3025; Mon. Sci. 1914, **4**, 5; Kunst. 1913, **3**, 196. F. P. 420682. D. R. P. Anm. B-65475, 1911; Kunst. 1913, **3**, 60. D. R. P. Anm. 68108, 1912; Kunst. 1913, **3**, 160. Belg. P. 251118, 1912; Kunst. 1913, **3**, 235.

[5] Rheinische Kunstseide Fabrik. D. R. P. 231652, 1909; abst. Zts. ang. Chem. 1911, **24**, 623; Chem. Zentr. 1911, I, 770; Wag. Jahr. 1911, II, 415; Kunst. 1911, **1**, 114; C. A. 1911, **5**, 2737. E. P. 18342, 1909 (O. Muller); abst. J. S. C. I. 1910, **29**, 557. D. R. P. 236537, 1908; abst. C. A. 1912, **6**, 1231; Wag. Jahr. 1911, II, 416; J. S. C. I. 1911, **30**, 1248; Zts. ang. Chem. 1911, **24**, 1499; Chem. Zentr. 1911, II, 326; Kunst. 1911, **1**, 295. F. P. 405571,

treating 1–3 parts of solid copper sulfate with 2–4 parts of a solution of NaOH of 21° Bé. and adding to the mixture 5–15 parts of aqueous ammonia of 25° Bé. The solution is then cooled to 0° and the crystals which form are separated. The liquid is said to be sufficient for dissolving one part of cellulose, the solvent being particularly applicable to the cellulose obtained from cottonseed hulls. E. Friedrich[1] replaces a portion or all of the ammonia by amines as monomethylamine or other alkylamine, producing soluble compounds with cellulose. W. Traube[2] advocates for the same purpose, aliphatic diamines as ethylene diamine, ethylenediaminotrimethylenediamine and tetramethylenediamine. M. Wassermann[3] advises to mix cuprous oxide with ammonium chloride which is then dissolved in ammonia at a

---

1909; abst. J. S. C. I. 1910, **29**, 417. D. R. P. 237816, 1910; addn. to D. R. P. 236537; abst. C. A. 1912, **6**, 1679; J. S. C. I. 1911, **30**, 1248; Zts. ang. Chem. 1911, **24**, 1988; Chem. Zentr. 1911, II, 1084; Wag. Jahr. 1911, II, 416; Kunst. 1911, **1**, 378. D. R. P. Anm. R-26760, R-29585. Belg. P. 218118, 1909. Aust. Anm. 5915, 1909.

[1] U. S. P. 850571, 1907; abst. J. S. C. I. 1907, **26**, 525. E. P. 27727, 1906; abst. J. S. C. I. 1907, **26**, 405. F. P. 372002, 1906; abst. J. S. C. I. 1907, **26**, 525. D. R. P. 189359, 1905; abst. Zts. ang. Chem. 1908, **21**, 1194; Chem. Zentr. 1908, I, 1119; Jahr. Chem. 1905–1908, II, 989; Chem. Ind. 1908, **31**, 141; Wag. Jahr. 1908, II, 354. U. S. P. 813878, 1906; abst. J. S. C. I. 1906, **25**, 280. E. P. 17164, 1905; abst. J. S. C. I. 1906, **25**, 950. F. P. 357171, 1906; abst. J. S. C. I. 1906, **25**, 88. U. S. P. 827434, 1906; abst. J. S. C. I. 1906, **25**, 845. E. P. 17381, 1905; abst. J. S. C. I. 1906, **25**, 586. F. P. 357172, 1905; abst. J. S. C. I. 1906, **25**, 70. D. R. P. 172264, 1904; abst. Wag. Jahr. 1906, II, 391. D. R. P. 172265, 1904; abst. Wag. Jahr. 1906, II, 391. Aust. P. 30705. Swiss P. 35080. E. P. 6072, 1906; abst. J. S. C. I. 1906, **25**, 1040. F. P. 364066, 1906; abst. J. S. C. I. 1906, **25**, 980. E. P. 12842, 1906; abst. J. S. C. I. 1907, **26**, 196. F. P. 366793, 1906; abst. J. S. C. I. 1906, **26**, 1091. D. R. P. 178410, 1905; abst. Zts. ang. Chem. 1907, **20**, 410; Wag. Jahr. 1907, II, 400. Aust. P. 31802. E. P. 21144, 1906; abst. J. S. C. I. 1907, **26**, 1045. F. P. 400221, 1909; abst. Mon. Sci. 1911, (5), **74**, 153. Can. P. 102233, 1906; 107979, 1907. Belg. P. 182289, 183058, 186471, 1905; 192529. 194741, 196219. 1906. Dan. P. 8258, 1906.

[2] W. Traube, U. S. P. 1064260, 1913; abst. J. S. C. I. 1913, **32**, 696; C. A. 1913, **7**, 2683; Mon. Sci. 1914, 23. E. P. 356, 1912; abst. J. S. C. I. 1912, **21**, 637; C. A. 1913, **7**, 2307. F. P. 438632, 1912; abst. J. S. C. I. 1912, **31**, 584; Kunst. 1912, **2**, 439. D. R. P. 245575, 1911; abst. C. A. 1912, **6**, 2316; J. S. C. I. 1912, **31**, 532; Zts. ang. Chem. 1912, **25**, 1034; Wag. Jahr. 1912, II, 439; Kunst. 1912, **2**, 176. D. R. P. 252661, 1911; addn. to D. R. P. 245575; abst. C. A. 1913, **3**, 416; Zts. ang. Chem. 1912, **25**, 2381; Kunst. 1912, **2**, 475; C. A. 1912, **6**, 2316. D. R. P. Anm. T-15850; abst. Kunst. 1912, **2**, 79, 240; T-16998, addn. to T-15850; T-16544, addn. to T-15850; abst. Kunst. 1912, **2**, 340. Aust. A-10798, 1911; abst. Kunst. 1912, **2**, 399. Swiss P. 58882, 1911. Belg. P. 241976, 245575, 252661, 1912; abst. Zts. Chem. Ind. Koll. 1912, **11**, 310.

[3] D. R. P. 274658, 1913; abst. C. A. 1914, **8**, 3374; Kunst. 1914, **4**, 234; Wag. Jahr. 1914, II, 336; Chem. Tech. Rep. 1914, **38**, 394; J. S. C. I. 1914, **33**, 785. Wassermann and Jaeger, Kunst. 1913, **3**, 117.

low temperature, caustic alkali being then added until a bright blue precipitate forms; this dissolves comparatively slowly in the cold, and is separated from the liquid which is then used as a cellulose solvent. It is claimed[1] that at least 6% NH_3 must be added to the Schweizer liquid. In the method of G. and A. Schaefer[2] the copper is subjected to the action of air and ammonia at a temperature changing alternately between —4° and +8°, and to the solution thus obtained the requisite amount of cupric sulfate and alkali are added, it being stated that 8–8.5 parts of a solution prepared in this manner containing about 8%–12% of ammonia and 45–50 gm. copper per liter will dissolve 1 part of cellulose. Where the cuprammonium solution is prepared by the action of sodium hydroxide upon copper sulfate with addition of ammonia, there is a tendency to the deposition of crystals of sodium sulfate. This is avoided in the O. Mueller[3] process by mixing the cupric salt with a solution of sodium chloride and glycerol before adding the ammonia and caustic alkali.[4] The La Soie Artificielle[5] start with copper sulfacetate and sodium carbonate.[6] The patented methods of E. de Haen,[7] E.

---

[1] J. Wetzel, F. P. 423510, 1910; abst. C. A. 1912, **6**, 2001; Mon. Sci. 1913, **79**, 117. F. P. 424293, 1911; abst. C. A. 1912, **6**, 2003.

[2] U. S. P. 879416, 884298, 1908; abst. J. S. C. I. 1908, **27**, 749; C. A. 1908, **2**, 2432; Mon. Sci. 1909, **69**, 28. Swiss P. 45321.

[3] F. P. 451406, 1913; abst. Mon. Sci. 1913, 7; C. A. 1913, **7**, 3227; Kunst. 1913, **3**, 213; J. S. C. I. 1913, **32**, 596; Rev. Chim. Ind. 1913, **24**, 189. D. R. P. 192690, 1905. D. R. P. Anm. M-47935, 1912; abst. Kunst. 1913, **3**, 180. Belg. P. 251128; abst. Kunst. 1913, **3**, 355.

[4] Example: 120 kilos. of powdered copper sulfate are stirred with 200 liters of a 1–2 per cent. solution of sodium chloride containing 2.25–3 liters of glycerol; to this are added 300 liters of ammonia, (sp. gr. 0.91,) and the copper salt is dissolved. Then 200 liters of caustic soda (sp. gr. 1.125–1.2) are added and 50 kilos. of cellulose finally introduced. See G. Fassbender, Ber. 1880, **13**, 1822.

[5] F. P. 437815, 1911; abst. J. S. C. I. 1912, **31**, 636; Kunst. 1912, **2**, 294. D. R. P. 252179; abst. Zts. Chem. Ind. Koll. 1912, **11**, 310. See Glanzfaeden Akt. D. R. P. 306107, 1918; abst. Chem. Zentr. 1918, II, 327.

[6] To 200 parts of this solution, about 14 parts of cellulose are added and allowed to steep until almost dissolved. After half an hour, 3 parts of caustic soda in 10 parts of water are added to the mixture and a perfect solution of the cellulose is thereby obtained.

[7] U. S. P. 1034235, 1912; C. A. 1912, **6**, 3018; Mon. Sci. 1913, **78**, 110; Kunst. 1913, **3**, 16; J. S. C. I. 1912, **31**, 811. E. P. 27835, 1911; C. A. 1913, **7**, 1972; J. S. C. I. 1912, **31**, 770. E. P. 4610, 1912; C. A. 1913, **7**, 2856; J. S. C. I. 1912, **31**, 1075. E. P. 6408, 1912; J. S. C. I. 1912, **31**, 981. E. P. 11613, 1912; C. A. 1913, **7**, 3662; J. S. C. I. 1912, **31**, 1120. F. P. 436968, 1911; J. S. C. I. 1912, **31**, 485; Kunst. 1912, **2**, 235. F. P. 440907, 1912; J. S. C. I. 1912, **31**, 812; Kunst. 1912, **2**, 353, 460. First addn. 15861, 1912, to F. P. 440907; Kunst. 1913, **3**, 53; J. S. C. I. 1912, **31**, 1120. F. P. 441063,

Mertz,[1] J. Ludlow and D. Mosher,[2] W. and V. Mahler,[3] W. Walenn and I. Timmis,[4] T. Eck,[5] F. Scheyn,[6] A. Chaumat,[7] Boettger,[8] and others[9] differ but little from the principles as above mentioned. To increase the stability of the cuprammonium solution a small amount of a polyhydric alcohol as glycerol or mannite,[10] grape sugar,[11] milk sugar or cane sugar,[12] or[13] an organic hydroxy compound, such as potassium sodium tartrate, and a little ammonium persulfate or other oxidizing agent may be added. J. Wetzel[14] claims to materially increase the stability and keeping qualities of a cuprammonium solution by reducing the amount of free am-

1912; J. S. C. I. 1912, **31**, 812. D. R. P. Anm. H-55092, 1911; Kunst. 1912, **2**, 240. D. R. P. Anm. H-56704, 1912; Kunst. 1912, **2**, 300. Belg. P. 241649, 1911; 243694, 243897, 245524, 1912; Kunst. 1912, **2**, 399. Holl. P. 585, 1912; C. A. 1913, **7**, 3239. Holl. P. 586, 1912; C. A. 1913, **7**, 3415. Consult Linkmeyer, F. P. 353187.

[1] F. P. 364911, 1906. Belg. P. 193002, 1906. U. S. P. 954984, 1910; abst. C. A. 1910, **4**, 1671; J. S. C. I. 1910, **29**, 627. L. Boneyds, Belg. P. 189754, 1906.

[2] U. S. P. 853986, 1907; abst. J. S. C. I. 1907, **26**, 688.

[3] Aust. Anm. A-3509, 1903. Aust. P. 18454, 1904.

[4] E. P. 6029, 1891.

[5] D. R. P. 240082, 1909; C. A. 1912, **6**, 2169; J. S. C. I. 1911, **30**, 1447; Zts. ang. Chem. 1911, **24**, 2334; Zts. Chem. Ind. Koll. 1912, **10**, 62; Chem. Zentr. 1911, II, 1567; Wag. Jahr. 1911, II, 417; Kunst. 1911, **1**, 454. D. R. P. Anm. E-18037, 1912; Kunst. 1913, **3**, 340, 400. D. R. P. Anm. E-14725, 1909; D. R. P. Anm. E-14902, 1909. E. Eck and E. Bechtel, U. S. P. 839825, 840611, 1907. T. Eck, E. Eck and F. Pollak, Belg. P. 210025, 1908. E. Elsaesser, E. P. 113010, 1917; abst. J. S. C. I. 1918, **37**, 146-A; C. A. 1918, **12**, 1256. Erste Oesterreichische Glanzstoff Fabr. A. G., Aust. P. A-781, 1905; abst. Mon. Sci. 1910, (4), **72**, 45.

[6] Belg. P. 187283, 1905.

[7] U. S. P. 1062222, 1913; C. A. 1913, **7**, 2472; J. S. C. I. 1913, **32**, 653; Mon. Sci. 1914, **4**, 23; Kunst. 1913, **3**, 417. E. P. 14525, 1899. F. P. 429841, 1910; J. S. C. I. 1911, **30**, 1308.

[8] Boettger, N. Rep. Pharm. **23**, 732; abst. Jahr. Chem. 1874, 878.

[9] A. DesMinieres, E. P. 2739, 1904; abst. J. S. C. I. 1904, **23**, 936. Comp. Francaise de la Soie Parisienne, F. P. 297278, 1900. Soc. Gen. Fabrication des Matières Plastiques, Aust. P. 2739, 1899. D. R. P. 113208. E. P. 14525, 1899.

[10] Chem. Fabr. Bettenhausen Marquart and Schulz, E. P. 4872, 1909; J. S. C. I. 1909, **28**, 1314. F. P. 399911, 1909; J. S. C. I. 1909, **28**, 938; Chem. Ztg. Rept. 1909, **33**, 472. Aust. P. 41720. Swiss P. 45290. Belg. P. 214426, 1909. See F. Flor and E. Murman, E. P. 14184, 1902.

[11] Vereinigte Glanzstoff Fabriken, Belg. P. 182386, 182455, 1905; 204557, 1907. E. P. 27707, 1907; abst. J. Soc. Dyers Col. 1909, **25**, 17.

[12] Soc. anon. francaise "La Soie Artificielle," E. P. 9253, 1908; abst. J. Soc. Dyers Col. 1909, **25**, 62.

[13] V. Mertz, U. S. P. 954984, 1910; abst. J. S. C. I. 1910, **29**, 627; C. A. 1910, **4**, 1671. F. P. 364911, 1907. Swiss P. 34760, 1906. F. P. 411592. E. P. 1148, 1909. Belg. P. 222298, 1910. (Brit. Cellulose Syndicate and V. Mertz.)

[14] F. P. 424293, 1910; abst. C. A. 1912, **6**, 2003. See also F. P. 423510, 1910; abst. J. S. C. I. 1911, **30**, 615. D. R. Anm. B-57073.

monia to 3%. M. Prud'homme has found[1] that an addition of caustic soda increases the solvent power of cuprammonium solutions for cellulose, four times the amount of copper present to cellulose being dissolved when two molecules of alkali are present to one molecule of copper salt. According to the Société anonyme "Le Crinoid,"[2] that portion of the cuprammonium solution which is in the colloid state exerts an especially energetic solvent power. Such colloid solutions may be obtained by dialysis as well as by treatment of copper salts with ammonia and alkalis provided the solution contains not to exceed two parts of cellulose for each part of cupric hydroxide in solution.

The quantities of cellulose which may be dissolved in solutions without the addition of foreign substances has been variously stated, variation being probably due to the preliminary (if any) treatment to which the cotton or other form of cellulose has been subjected. Fremery and Urban[3] found that ordinary or untreated cellulose dissolves in cuprammonium solution to the extent of only 4%, while in the Pauly patent[4] is stated that 45 gm. of cellulose dissolves in one liter of cuprammonium solution containing 15 gm. copper per liter, the time required to effect complete solution being given as eight days. Both low temperature and high copper content are conducive to most rapid and complete solution.

E. Grimaux[5] has studied the dialysis of these copper solutions and came to the conclusion that it was the non-dialyzable portion of the solution of copper hydroxide in ammonia which acted as a solvent for the cellulose.

All solutions of ammoniacal cupric oxide possess the defect that on exposure to the atmosphere they readily decompose, cupric oxide is deposited, and their solvent power toward cellu-

---

[1] F. P. 344138, 1904; abst. J. S. C. I. 1904, **23**, 1087. See Dingl. Poly. 1872, **204**, 514; Chem. Tech. Mitth. 1871–1872, 34.

[2] F. P. 401741, 1902; abst. J. S. C. I. 1909, **28**, 1121. E. P. 14143, 1908; abst. J. S. C. I. 1909, **28**, 880; J. Soc. Dyers Col. 1909, **25**, 246. U. S. P. 947715; abst. C. A. 1910, **4**, 152.

[3] D. R. P. 111313, 1899; abst. Wag. Jahr. 1900, II, 448; Chem. Centr. 1890, II, 550. U. S. P. 646381, 657818. E. P. 6557, 1899. F. P. 278371, 286925. Aust. 3636.

[4] D. R. P. 98642; abst. Wag. Jahr. 1903, II, 417; Jahr. Chem. 1898, 1370; Chem. Centr. 1898, II, 911. F. P. 272718. E. P. 28631, 1897. U. S. P. 617009.

[5] Compt. rend. 1884, **98**, 1434; abst. Bull. Soc. Chim. 1884, **42**, 156; J. C. S. 1884, **46**, 957. See also Peligot, Ann. Chim. Phys. 1861, (3), **13**, 343.

lose correspondingly diminished. The decomposition increases with rise in temperature, whereas the solubility of the cellulose diminishes as the temperature becomes higher. Various proposals for obviating this defect have been made, such as the addition of an electro-negative insoluble metal, oxygen, ozone, and carbohydrates and polyvalent alcohols. Glycerol, acetol, potassium sodium tartrate or ammonium persulfate[1] have also proved suitable.

Attention is drawn to the fact that cuprammonium hydroxide is not as strong an alkali as sodium hydroxide. Levallois[2] has stated that the solution of cellulose in cuprammonium is optically active, which statement is not substantiated by Bechamp.[3] The solutions of cellulose in hydrochloric acid, however, aqpear to be optically inactive.[4]

After the artificial filament has been forced through the spinneret, it is precipitated or coagulated by immersion in acid or alkaline baths, dextrin,[5] diastase,[6] starch,[7] soluble arsenites,[8]

---

1. British Cellulose Syndicate and V. Mertz, E. P. 1148, 1909. Belg. P. 222298; 1910; J. S. C. I. 1910, **29**, 24. F. P. 411592. U. S. P. 954984; abst. J. S. C. I. 1910, **29**, 627.
2. Bull. Soc. Chim. 1885, (2), **43**, 83; Ber. 1885, **18**, 64; J. C. S. 1884, **46**, 1288; Compt. rend. 1884, **98**, 732; 1884, **99**, 431, 1027.
3. Compt. rend. 1884, **99**, 1027, 1122; 1885, **100**, 279, 368; Ber. 1885, **18**, 113.
4. R. Willstätter and L. Zechmeister, Ber. 1913, **46**, 2401; abst. C. A. 1913, **7**, 3412; J. S. C. I. 1913, **32**, 822; J. C. S. 1913, **104**, i, 955; J. Soc. Dyers Col. 1913, **29**, 326; Bull. Soc. Chim. 1913, **14**, 1354; Chem. Zentr. 1913, II, 1209.
5. J. Delpech, F. P. 437014, 1911; J. S. C. I. 1912, **31**, 485; Kunst. 1912, **2**, 233. See Thomas and Bonavita, F. P. 302908, 1900.
6. E. Legrand, E. P. 19001, 1912; abst. C. A. 1914, **8**, 571; J. S. C. I. 1913, **32**, 907; J. Soc. Dyers Col. 1913, **29**, 326. D. R. P. 250357, 1911; abst. C. A. 1913, **7**, 246; J. S. C. I. 1912, **31**, 1120; Kunst. 1912, **2**, 319, 353; Zts. ang. Chem. 1912, **25**, 2381; Wag. Jahr. 1912, II, 441. F. P. 445896, 1911; abst. J. S. C. I. 1912, **31**, 1176. U. S. P. 1130830; abst. C. A. 1915, **9**, 1123. E. P. 5154, 1913, addn. to E. P. 19001, 1912; abst. C. A. 1914, **8**, 2258; J. Soc. Dyers Col. 1913, **29**, 326; J. S. C. I. 1913, **32**, 907. F. P. 17170, 1912, addn. to F. P. 445896, 1911; abst. C. A. 1914, **8**, 822; J. S. C. I. 1913, **32**, 865; Kunst. 1913, **3**, 332. D. R. Anm. L-33200, 1911.
7. L. Cuntz, F. P. 383411, 383412, 383413, 1907; abst. J. S. C. I. 1908, **27**, 331.
8. Comp. Français Des Applications de La Cellulose, E. P. 27878, 1910; C. A. 1912, **6**, 1526; J. S. C. I. 1911, **30**, 1236, 1309. E. P. 28779, 1910; C. A. 1912, **6**, 1526; J. S. C. I. 1911, **30**, 1236. E. P. 11714, 1911; C. A. 1912, **6**, 3183; J. S. C. I. 1912, **31**, 428; Kunst. 1912, **2**, 296. F. P. 422565, 1910; J. S. C. I. 1911, **30**, 532; Kunst. 1911, **1**, 276. F. P. 429841, 1910; J. S. C. I. 1911, **30**, 1309; Kunst. 1911, **1**, 455. F. P. 440776, 1911; J. S. C. I. 1912, **31**, 812; Kunst. 1912, **2**, 460. D. R. P. 252180, 1911; abst. C. A. 1913, **7**, 416; Zts. ang. Chem. 1912, **25**, 2381; Wag. Jahr. 1912, **58**, II, 443; Kunst. 1912, **2**, 399. Aust. A-4369, 1911. Swiss P. 57951; Kunst. 1913, **3**,

alkaline carbonates,[1] or hexoses, saccharobioses and polysaccharides.[2] Sodium ricinoleate has been proposed as an addition to soften the filaments.[3]

In addition to filament formation, the cuprammonium celluloses have been extensively employed in the waterproofing of textiles, and qaper as in the processes of C. Hime and J. Noad,[4] A. Healey and J. Williams,[5] who developed the "Willesden goods," J. Inglis,[6] E. Krusche,[7] A. Maltman,[8] Y. Murrow,[9] C. Snell,[10] C. Baswitz[11] and J. Williams.[12] In the manufacture of incandescent

213. Belg. P. 237056, 1911; D. R. P. Anm. C-20719, 1911; abst. Kunst. 1912, **2**, 260.

[1] Le Crinoid Soc. Anon. E. P. 21191, 1908; abst. J. S. C. I. 1909, **28**, 1194; J. Soc. Dyers Col. 1909, **25**, 313. E. P. 22413, 1909; abst. J. S. C. I. 1910, **29**, 1053. F. P. 410827, 1909; abst. J. S. C. I. 1910, **29**, 810; Mon. Sci. 1911, (5), **74**, 155. U. S. P. 980294, A. Lecoeur and P. Rudolf, F. P. 201741, 1909. F. P. 401741, 1909. F. P. 392869. See also A. Lecoeur.

[2] P. Freidrich, Swiss P. 45764, 48576, 1909. Belg. P. 217548, 221951, 1909. D. R. P. 206883, 1907; abst. Chem. Zentr. 1909, I, 213; Papierfabr. 1909, **7**, 210. Belg. P. 210489, 1908; 214932, 216802, 217548, 1909. Marquart and Schulz, Swiss P. 45290, 1909.

[3] E. Bechtel, U. S. P. 988430, 1911. U. S. P. 1066785, 1913; abst. J. S. C. I. 1913, **31**, 785; Mon. Sci. 1914, **33**, 23; C. A. 1913, **7**, 3031. D. R. P. 220711, 1907; abst. J. S. C. I. 1910, **29**, 556; Chem. Zentr. 1910, I, 1474; Wag. Jahr. 1910, II, 428; C. A. 1910, **4**, 2209; Jahr. Chem. 1910, 427. D. R. P. 225549, 1909; J. S. C. I. 1913, **32**, 420; C. A. 1911, **5**, 2176. D. R. P. 229711, 1909; Wag. Jahr. 1911, II, 413; Kunst. 1911, **1**, 74; Zts. ang. Chem. 1911, **24**, 189; Chem. Zentr. 1911, I, 279; C. A. 1911, **5**, 2554. D. R. P. 255549, 1911; abst. J. S. C. I. 1913, **32**, 420.

[4] C. Hime and J. Noad, U. S. P. 456821, 1891. E. P. 7715, 7716, 1889. Belg. P. 86160, 1889. F. P. 198076, 1889. D. R. P. 50936, 1889. Can. P. 32739, 1889. Victoria P. 7278, 1889. N. South Wales P. 1859, 1889. Turkey P. 158, 1889. New Zealand P. 4095, 1889. Ital. P. Dec. 5, 1889, LII, 103. Cape of Good Hope P. Dec. 17, 1889, C. D. 28. Natal P. Dec. 18, 1889. Tasmania P. Dec. 23, 1889, No. 780/10. S. Australia P. 1486, 1889. S. Africa Repub. P. 141, 1889. Brazil P. 813, 1889. Queensland P. 910, 1889. Span. P. 10241, 1889. Aust.-Hung. P. 44671, 1890. India P. March 28 and April 24, 1890. Straits Settlements P. May 2, 6, 1890. Ceylon P. 345, 1890. Hong-Kong P. June 13, 1890. Port. P. 1539, 1891.

[5] A. Healey, E. P. 3685, 1877; 185, 1878; 5054, 1894; abst. J. S. C. I. 1895, **14**, 381. D. R. P. 14717, 1894; abst. Wag. Jahr. 1881, 93; Mon. Sci. 1894, **44**, 167.

[6] J. Inglis, E. P. 101894, 1916; abst. C. A. 1917, **11**, 542; J. S. C. I. 1916, **35**, 1257.

[7] E. Krusche, D. R. P. 106043; abst. Wag. Jahr. 1900, II, 449; Chem. Centr. 1900, I, 639; Jahr. Chem. 1900, 846.

[8] E. P. 104986, 1916; abst. J. S. C. I. 1917, **36**, 544; C. A. 1917, **11**, 2155.

[9] E. P. 1063, 1874.

[10] E. P. 10107, 1888.

[11] E. P. 16708, 20665, 1889; abst. J. S. C. I. 1890, **9**, 1047; 1891, **10**, 133.

[12] E. P. 1358, 12309, 1889; 20524, 1889; abst. J. S. C. I. 1890, **9**, 742; 1891, **10**, 157. U. S. P. 444515, 1891. E. P. 19013, 1901; abst. J. S. C. I. 1902, **21**, 1132.

gas mantles from cuprammonium cellulose, the patented processes of R. Langhans,[1] and the work of A. Mueller,[2] W. Bruno[3] and G. Drossbach & Co.,[4] may be cited. D. von Monckhoven has proposed to utilize the cellulose for photographic films,[5] but the process has never been successfully commercially exploited. As substitutes for rubber,[6] in the waterproofing of wood,[7] as an ingredient in cements, sizes and finishes,[8] to render corks impermeable and water-resistant,[9] for artificial leather[10] and bone,[11] and plastic masses,[12] are some of the fields of usefulness which have been proposed for the cellulose regenerated from ammoniacal copper solutions. Attempts to combine cuprammonium cellulose with natural silk and fibroin, as in the processes of E.

---

1. Chem. Tech. Rep. 1895, **34,** II, 127. U. S. P. 672946, 1901; abst. Mon. Sci. 1901, (4), **57,** 283. D. R. P. 140347; abst. Wag. Jahr. 1904, II 389; Jahr. Chem. 1903, 1013. D. R. P. 115068; abst. Wag. Jahr. 1901, I, 93

2. Zts. ang. Chem. 1906, **19,** 1810; abst. C. A. 1907, **1,** 355; Jahr Chem. 1905–1908, I, 2217.

3. Zts. ang. Chem. 1906, **19,** 1387; abst. C. A. 1907, **1,** 481; see also 1907, **1,** 355; Jahr. Chem. 1905–1908, 2217.

4. Zts. ang. Chem. 1906, **19,** 1427; abst. Chem. Centr. 1906, II, 1147. See also D. R. P. 117755, 1899; abst. Chem. Centr. 1901, I, 546.

5. Compt. rend. 1859, **48,** 648; abst. Poly. Centr. 1859, **25,** 813; see also Poly. Centr. 1858, 427. Eder's. Hand. Phot. 1896, **2,** II, 344.

6. J. Gebauer, F. P. 415996; abst. Kunst. 1911, **1,** 92. P. and G. Marino, E. P. 22303, 1901. C. Steinmetz, U. S. P. 669358, 1901; abst. Kunst. 1913, **3,** 390. E. P. 21293, 1900. O. Wheeler, U. S. P. 1049955, 1913; abst. C. A. 1913, **7,** 906; Kunst. 1913, **3,** 218; Mon. Sci. 1913, **78,** 107.

7. J. Gerlache, E. P. 8176, 1909; abst. J. S. C. I. 1910, **29,** 568. H. Monseur, E. P. 23139, 1911; abst. J. S. C. I. 1913, **32,** 235. D. Whitehead and Q. Marino, E. P. 20143, 1905; abst. J. S. C. I. 1906, **25,** 1052.

8. C. Schwalbe, Zts. Chem. Ind. der Kolloide, 1908, **2,** 229; abst. J. S. C. I. 1908, **27,** 278. J. Scoffern, E. P. 1744, 1859; 1380, 1717, 1868. Annal. du Genie Civil, 1869, 613; Mon. Sci. 1870, 34; Dingl. Poly. **95,** 95; Chem. Centr. 1870, 34; Poly. Centr. 1869, 1596. J. Scoffern and G. Tidcombe, E. P. 827, 1875. Sedlaczek, Kunst. 1911, **1,** 143; abst. Chem. Ztg. 1912, **36,** 196; Wag. Jahr. 1911, II, 143. G. Brabrook, U. S. P. 1244463, 1917; abst. J. S. C. I. 1918, **37,** 15-A.

9. L. Pink, U. S. P. 1056446, 1056447, 1913. E. P. 2455, 1911. Can. P. 133161, 1911. D. R. P. Anm. A-711, 1911. See also Nat. Drug. 1912, **10,** 465.

10. R. Lissauer, U. S. P. 586907, 1897.

11. R. Reiman, U. S. P. 494891, 1893.

12. L. Collardon, U. S. P. 953319, 1910; Dingl. Poly. 1872, **204,** 514; abst. J. C. S. 1872, **25,** 1137. P. Isherwood, E. P. 16364, 1906. L. Jumau, E. P. 27120, 1906. King's Norton Metal Co., T. Bayliss, H. Brownsdon and H. Smith, E. P. 13297, 1905; 7472, 1910. Mertens & Co. and H. Jerosch, E. P. 18493, 1908. A. Paraf, E. P. 219, 1868. R. Seeman, E. P. 18864, 1900. Soc. Anon. Française la Soie Artificielle, F. P. 385083, 1907; abst. J. S. C. I. 1908, **27,** 558; C. A. 1909, **3,** 1094. F. P. 385083, 1907; and addn. 9253, 1908; abst. J. S. C. I. 1908, **27,** 1057.

Galbert[1] and P. Follet and G. Ditzler,[2] have in the main, been unsuccessful.

Physical Constants of Cuprammonium Solutions. F. Donnan and J. Thomas[3] have determined at 25° the solubility of crystalline cuprous oxide in solutions of ammonia of varying concentrations, and have found that for a certain range of ammonia concentration, the amount of total copper dissolved is approximately proportional to the square root of the "free" ammonia. From this result the conclusion is drawn that in these solutions the cuprous-ammonium hydroxide present, is mainly of the type $(Cu.NH_3)OH$.

In the experiments made on the solubility of cellulose in ammoniacal copper hydroxide and on the relationships existing between the concentration of ammonia, copper and the quantity of cellulose dissolved, as carried out by E. Connerade,[4] it is shown that a solution of ammoniacal cuprous hydroxide prepared at low temperatures contains—in comparison with cupric hydroxide

---

1. F. P. 440846, 1911; J. S. C. I. 1912, **31**, 811; Kunst. 1912, **2**, 333, 460. F. P. 442117, 1911; abst. J. S. C. I. 1912, **31**, 917; Kunst. 1912, **2**, 347.

2. E. P. 22753, 1907; J. S. C. I. 1908, **27**, 19. E. P. 21285, 1908; J. S. C. I. 1909, **28**, 87. F. P. 382859, 1907; J. S. C. I. 1908, **27**, 221; C. A. 1909, **3**, 1093; Mon. Sci. 1908, (4), **68**, 166. F. P. 395223, 1908; J. S. C. I. 1909, **28**, 307. D. R. P. 210280, 211871, 1906; abst. C. A. 1909, **3**, 2630. D. R. P. 223294, 1907; addn. to D. R. P. 211871, 1906. D. R. P. 229677, 1908; C. A. 1911, **5**, 2535; J. S. C. I. 1911, **30**, 210; Zts. ang. Chem. 1911, **24**, 183; Chem. Zentr. 1911, I, 274. Belg. P. 190636, 1906; 203196, 1907. Aust. P. 43640. Swiss P. 41238, 44075. F. Beltzer, Kunst. 1912, **2**, 223. B. Bilitt, Le Genie Civil, 1909, **15**, 451; Chem. Ztg. Rept. 1910, **34**, 23. H. Blackmore, U. S. P. 803391, 1905; abst. J. S. C. I. 1905, **24**, 1226. H. Boistesselin and C. Gay, F. P. 403193, 1909. J. Brandenberger, D. R. P. Anm. B-62509, 1911. Chem. Fabr. von Heyden, Belg. P. 232475, 1911. Cramer and Wiesner, Chem. Tech. Rep. Jacob. 1871, **10**, I, 66. R. Freemantle, D. R. P. 137461; Wag. Jahr. 1903, II, 415. See Wag. Jahr. 1901, 513. J. Foltzer, Kunst. 1911, **1**, 301, 390, 404, 427. See J. Foltzer, Belg. P. 189918, 1906. Fremery, Rev. Ind. **21**, 264. La Soie Artificielle Soc. Anon. Francaise, E. P. 1573, 1912. E. Richard, Zts. Farben Ind. 1910, **9**, 361; abst. Jahr. Chem. 1910, 428. H. Riesenfeld and F. Traube, Ber. 1905, **38**, 2798; abst. Wag. Jahr. 1905, II, 396; Jahr. Chem. 1905–1908, 987. W. Vieweg, International Congress, London; abst. Zts. ang. Chem. 1909, **22**, 1119. H. Vogel, J. Appl. Chem. Sept. 1872; abst. Am. J. Pharm. 1872, **44**, 518. M. Weertz, E. P. 12422, 1910; abst. J. S. C. I. 1911, **30**, 798. See also Ding. Poly. 1874, **204**, 514; abst. Chem. Centr. 1872, 827. Chem. Tech. Rep. 1872, **11**, I, 105. Neues Erfindungen unt Erfahrungen, 1874, **1**, 516. C. N. 1880, **41**, 284. Cosmos, 1899, **40**, 450. Mon. Sci. 1908, (4), **68**, 657. F. P. 436936, 1911.

3. F. Donnan and J. Thomas, Proc. Chem. Soc. 1911, **27**, 213; J. C. S. 1911, **99**, 1788; J. S. C. I. 1911, **30**, 1250.

4. E. Connerade, Bull. Soc. Chim. Belg. 1914, **28**, 176; J. S. C. I. 1914, **28**, 744; C. A. 1915, **9**, 861; J. C. S. 1914, **106**, i, 932. A. Droste, Belg. P. 191200, 1906. E. Legrand, Belg. P. 248521, 1912.

—a large excess of colloidal ammonium cuprous hydroxide. According to this investigator, the solubility of cellulose is directly proportional to the concentration of the colloidal cuprammonium solution. The solution of the cellulose is best brought about by the combination of quantities of colloidal ammoniacal cuprous hydroxide and water in amounts which increase to a point at which an equilibrium exists between the liquid and solid phases. It is alleged that the strongly hydrated colloidal complex combines with ammonia in proportion to its concentration, which tends to render the complex more stable. Furthermore, the coagulation of the colloidal complex can be effected reversibly in solution.

Bouzat[1] has prepared a number of crystallized cuprammonium salts. The compound $CuCl_2.5NH_3.{}^3/_2H_2O$ is prepared by cooling an ammoniacal solution of cupric chloride to —15°, or by passing ammonia gas into the solution at 0°; it forms small dark blue crystals, soluble in water. In presence of a large quantity of water, cupric hydroxide separates. On heating, the compound $CuCl_2.2NH_3$ is formed. On standing over caustic potash in an atmosphere of ammonia, the salt loses 1 mol. of water, forming the compound $CuCl_2.5NH_3.{}^1/_2H_2O$.

The salt $CuCl_2.4NH_3.2H_2O$ is produced by allowing an ammoniacal solution of cupric chloride to evaporate at the ordinary temperature in an atmosphere of ammonia, or by treating a concentrated, hot, ammoniacal solution of cupric chloride with alcohol, and allowing to cool. It forms dark blue crystals and has properties similar to the above-mentioned compound.

The salt $CuCl_2.2NH_3.{}^1/_2H_2O$ is obtained by heating an ammoniacal solution of cupric chloride to 50° and then incompletely precipitating with hot alcohol. It forms bluish green microscopic crystals smelling faintly of ammonia. Like the corresponding anhydrous salt, it is decomposed by water.

The cuprammonium sulfate $CuSO_4.4NH_3.{}^3/_2H_2O$ can be prepared by allowing an ammoniacal solution of copper sulfate to evaporate over lime; by precipitating such a solution with alcohol; by allowing a similar hot concentrated solution to cool; or by passing ammonia into such a solution. It has similar prop-

---

[1] Ann. Chim. Phys. 1903, (7), **29**, 305; abst. Chem. Centr. 1903, II, 417; J. S. C. I. 1903, **22**, 1045. See also J. S. C. I. 1902, **21**, 932, 970, 1158.

erties to the chloride, $CuCl_2.4NH_3.{}^3/_2H_2O$, but less energetic.

The author has determined the thermo-chemical relations of these salts, and also of the two double salts

$CuSO_4.(NH_4)_2SO_4.6H_2O$ and $CuCl_2.2NH_4Cl.2H_2O$.

Bouzat[1] has also investigated the effect of adding bases to ammonio-cupric salts, and of adding ammonio-cupric hydroxide to salts of these bases, by determining the resulting thermal changes. The ammonio-cupric base displaces ammonia completely from its salts, while ammonia has no effect on the ammonio-cupric salt. In the case of potash and the ammonio-cupric salt (or ammonio-cupric base and potassium salt) there is partition, the potash taking the greater part of the acid; but the amount of ammonio-cupric salt increases as the excess of ammonia present increases. This partition is shown also by adding potash to a solution of ammonio-cupric salt, which then acquires the power (possessed by the base but not by its salts) of dissolving cellulose; or by adding a potassium salt to a solution of cellulose in ammonio-cupric hydroxide, when some of the cellulose is precipitated. In the case of lime (or calcium salts) there is also partition; but when the ammonio-cupric liquor is strongly ammoniacal, it will displace lime almost completely from calcium salts, forming a considerable precipitate of lime in the liquid. The ammonio-cupric hydroxide is thus shown to be a very strong base.

When the ammoniacal solution of cupric hydroxide in excess of ammonia is allowed to stand over sulfuric acid until a precipitate begins to appear, the product has the composition expressed by $CuO.25NH_3$. Bouzat[2] has made calorimetric measurements on the neutralization by acids of the solution $CuO.28NH_3$, and concludes that the base is formed from copper oxide and ammonia with slight evolution of heat, and that, when formed, it is a strong base, much more energetic than ammonia.

Schützenberger and Riesler[3] have stated that ammoniacal cuprous oxide absorbs, when shaken with water containing air,

---

1. Compt. rend. 1902, **134**, 1502; abst. J. S. C. I. 1902, **21**, 970. See the researches of E. Connerade, Bull. Soc. Chim. Belg. 1914, **28**, 176; Zts. Chem. Ind. Koll. 1915, **16**, 95.
2. Compt. rend. 1902, **134**, 1310; abst. J. S. C. I. 1902, **21**, 932; J. C. S. 1903, **84**, ii, 21; Chem. Centr. 1902, II, 185; Jahr. Chem. 1902, 668.
3. Ber. 1873, **6**, 678; Bull. Soc. Chim. 1873, **19**, 152; **20**, 145; Compt. rend. 1873, **76**, 440, 1214; Jahr. Chem. 1873, 981.

twice the amount of oxygen necessary to convert it into cupric oxide, and have accounted for this, by assuming the formation of hydrogen peroxide or some similar body. J. Meyer[1] has prepared an ammoniacal cuprous solution by adding ammoniacal sulfate to a boiling solution of sodium sulfite without access of air, when the reduction occurs rapidly and quantitatively. This solution is converted quantitatively by hydrogen peroxide into the cupric condition, so that the two substances cannot co-exist. Moreover, when shaken up with a known volume in excess of moist air, it absorbs exactly the amount needed to convert it into the cupric solution. The author considers that, Schützenberger's results are due to the fact that he prepared his cuprous salt by reducing a cupric salt with sodium thiosulfate; he thus produced cuprous salt and sulfite, and the absorption of the excess oxygen was effected by the sulfite so produced. Direct experiments show that the oxidation of sulfite by moist air is greatly accelerated by the presence of cupric salts. Arsenites are not similarly oxidized. Possibly the process of oxidation may consist in the formation of a cupric peroxide, which at once oxidizes more cuprous oxide ($2Cu_2O + O_2 = Cu_2O_3 + Cu_2O = 4CuO$), or may oxidize sulfur dioxide if that be present ($Cu_2O + O_2 + SO_2 = Cu_2O_3 + SO_2 = 2CuO + SO_3$).

In his investigations of the manufacture of cuprammonium filaments by the Linkmeyer process,[2] W. Normann[3] has found

---

[1] Ber. 1902, **35**, 3952; abst. J. S. C. I. 1902, **21**, 154. C. Guignet has shown (Compt. rend. 1889, **109**, 528; abst. J. C. S. 1889, **56**, 1133) that dry starch or flour readily absorbs cuprammonium solution, decolorizing the liquid. Starch paste acts in an analogous manner, but the color is rapidly lost. A deep blue compound is formed from which water and even dilute ammonia remove only traces of copper. It retains ammonia if heated with water to 40°, the solution becoming pale blue. At 80° starch paste begins to form, but retains cupric oxide so tenaciously that under microscopic examination each starch granule is observed to be covered with a dark gray pellicle. Inulin behaves in a similar manner.

[2] R. Linkmeyer, U. S. P. 795526, 1905; abst. J. S. C. I. 1905, **24**, 887. E. P. 4755, 1905; abst. J. S. C. I. 1906, **25**, 371. E. P. 4756, 1905. F. P. 346722, 1904; abst. Wag. Jahr. 1905, II, 396; J. S. C. I. 1905, **24**, 238. D. R. P. 183153, 1904, abst. Wag. Jahr. 1907, II, 394; Zts. ang. Chem. 1907, **20**, 1542; Chem. Zentr. 1907, II, 1033; Chem. Tech. Rep. 1907, **31**, 210; Mon. Sci. 1909, (4), **70**, 166; Jahr. Chem. 1905–1908, 988. Aust. P. 46701. U. S. P. 796740, 1905; abst. J. S. C. I. 1905, **24**, 966. F. P. 352528, 1905; abst. J. S. C. I. 1905, **24**, 967; Mat. Col. 1905, **9**, 339. E. P. 6356, 1905; abst. J. S. C. I. 1905, **24**, 967. D. R. P. 169906; abst. Wag. Jahr. 1906, II, 386. Swiss P. 35434. Aust. P. 28595. U. S. P. 839013, 839014, 1906; abst. J. S. C. I. 1907, **26**, 197. F. P. 356402, 1905; abst. J. S. C. I. 1905, 24, 1300. E. P. 4761, 1905; abst. J. S. C. I. 1905, **24**, 671; Wag. Jahr. 1905,

that the coagulated thread, instead of becoming milky white as is the case when an acid coagulating bath is used, remains blue and perfectly transparent. This is due to the formation of a copper alkali cellulose, by the displacement of ammonia by soda in the cellulose compound. Cupric hydroxide dissolves to a slight extent in concentrated soda lye giving a blue solution. If cotton be immersed in this solution the ordinary phenomena of

II, 396. U. S. P. 842568, 1907; abst. J. S. C. I. 1909, **28**, 406. E. P. 4765, 1905; abst. J. S. C. I. 1906, **25**, 371. F. P. 361061, 1905; abst. J. S. C. I. 1906, **25**, 692. U. S. P. 857640, 1907; abst. J. S. C. I. 1907, **26**, 808. E. P. 3549, 1906; abst. J. S. C. I. 1906, **25**, 1090. U. S. P. 852126, 1907; abst. J. S. C. I. 1907, **26**, 606. D. R. P. 183557; abst. Jahr. Chem. 1905–1908, 988; Wag. Jahr. 1907, II, 394; Chem. Zentr. 1907, II, 1034; Chem. Tech. Rep. 1907, **31**, 245. D. R. P. 187313, addn. to D. R. P. 183557; abst. Jahr. Chem. 1905–1908, 988; Wag. Jahr. 1907, II, 195, 394; Chem. Zentr. 1907, II, 1768; Chem. Tech. Rep. 1907, **31**, 423; see also E. P. 4755, 1905. U. S. P. 866371. E. P. 3566, 1906; abst. J. S. C. I. 1907, **26**, 252. F. P. 353187, 1905; abst. J. S. C. I. 1905, **24**, 1011. D. R. P. 184150; abst. Jahr. Chem. 1905–1908, 988; Wag. Jahr. 1907, II, 395; Chem. Zentr. 1907, II, 1034; Chem. Tech. Rep. 1907, **31**, 245. Aust. P. 35268. Swiss P. 40614 (R. Linkmeyer and M. Pollak). U. S. P. 945559, 1910. E. P. 4104, 1909 (P. Friederich); abst. J. S. C. I. 1909, **28**, 934. U. S. P. 962769, 1910; abst. J. S. C. I. 1910, **29**, 941; see also P. Friederich, D. R. P. 206883, 1907; abst. J. S. C. I. 1909, **28**, 362. U. S. P. 962769, 962770, 1910; abst. J. S. C. I. 1910, **29**, 941. E. P. 14112, 1909; abst. J. S. C. I. 1910, **29**, 622. F. P. 404372. D. R. P. 206883; see also P. Freiderich, Swiss P. 48679. U. S. P. 979013, 1910. U. S. P. 1000827, 1911; abst. C. A. 1911, **5**, 3700. U. S. P. 1022097, 1912; abst. Kunst. 1912, **2**, 354; C. A. 1912, **6**, 1675; J. S. C. I. 1912, **31**, 429. F. P. 409789, 1909; abst. J. S. C. I. 1910, **29**, 750. U. S. P. 1062106, 1913; abst. J. S. C. I. 1913, **32**, 653. E. P. 11700, 1909; abst J. S. C. I. 1909, **28**, 1246; C. A. 1913, **7**, 2472. E. P. 1501, 1905; 4746, 1905; abst. J. S. C. I. 1906, **25**, 473. F. P. 347960, 1904; abst. Mat. Col. 1905, **9**, 209; J. S. C. I. 1905, 428. F. P. 346722, 1904; abst. Zts. ang. Chem. 1905, **28**, 1108; Bay. Ind. Gew. Blatt. 1905, **37**, 367. F. P. 350889, 352530, 1905; abst. Mat. Col. 1905, **9**, 339. E. P. 6357, 1905. Swiss P. 35435. F. P. 357837, 1905; abst. J. S. C. I. 1906, **25**, 120. D. R. P. 168830, 1904. Aust. P. 28581. D. R. P. 175296, 1904; abst. Mon. Sci. 1908, (4), **68**, 160; Zts. ang. Chem. 1907, **20**, 461; Chem. Tech. Rep. 1906, **30**, 334; Chem. Zts. 1906, **6**, 9; Wag. Jahr. 1906, II, 387. Aust. P. 30449. D. R. P. 183557, 1904. D. R. P. 185139, addn. to D. R. P. 175296, 1904; abst. Wag. Jahr. 1907, II, 395; Zts. ang. Chem. 1907, **20**, 1542; Chem. Zentr. 1907, II, 1039; Chem. Tech. Rep. 1907, **31**, 303. D. R. P. 185139, addn. to D. R. P. 176296, 1904. D. R. P. 222131; abst. Wag. Jahr. 1910, II, 436; Chem. Zentr. 1910. II, 51. D. R. P. 249002, 1911; abst. Kunst. 1912, **2**, 352; Wag. Jahr. 1912, II, 437. Belg. P. 181359, 181360, 1906; 183197, 183198, 186698, 188519, 1905. Can. P. 94977, 94978, 1905; 101114, 1906. Neues. Erfindungen und Erfahrungen 1906, **33**, 130. R. Linkmeyer and M. Pollak, F. P. 350888, 1905; abst. J. S. C. I. 1905, **24**, 800; Mat. Col. 1905, **9**, 309. E. P. 1501, 1905; abst. J. S. C. I. 1905, **24**, 670. F. P. 350889, 1905; abst. J. S. C. I. 1905, **24**, 888. Swiss P. 40164, 1907. See also, F. P. 347960; abst. J. S. C. I. 1905, **24**, 438. Belg. P. 181944, 181945, 1905.

3. W. Normann, Chem. Zts. 1906, **30**, 47, 584; abst. Gummi. Ztg. Celluloid Suppl. 1906, **21**, 3; J. S. C. I. 1906, **25**, 652; Jahr. Chem. 1905–1908, 987; Chem. Centr. 1906, II, 719; Zts. anorg. Chem. 1905, **41**, 132.

mercerization are observed, but at the same time the fiber is colored deep blue, and the liquid is decolorized. By repeatedly renewing the copper solution a saturation point is reached at which the cellulose ceases to absorb more copper. The compound can then be washed without dissociation by means of soda lye of a certain strength, and analysis shows a ratio of cellulose to copper in the saturated compound corresponding to the formula $C_{12}H_{20}O_{10}.CuO$, or 23.15% of copper oxide. The copper-alkali-cellulose compound is dissociated by water, pale blue copper hydroxide being precipitated in the thread. The precipitation of a cuprammonium solution of cellulose by substitution of the alkali requires a certain concentration of the soda lye; conversely the soda in the coagulum can be displaced if a large excess of concentrated ammonia be employed, and the soluble ammonium compound is regenerated. Consequently copper-alkali cellulose can be produced in solutions rich in copper by adding sufficient caustic soda lye to a solution of cuprammonium. The threads of artificial silk coagulated in a caustic soda bath, and washed in soda lye are deep blue in color; the copper is immediately removed by dilute acids, and the decolorized threads retain their perfect transparency. Additional work has been done upon this subject by W. Bonsdorff,[1] G. Bodlaender and R. Fittig,[2] K. Koelichen,[3] E. Berenguer,[4] R. Trierenberg,[5] W. Minajeff,[6] H. Ost,[7] A. Herzog,[8] E. Berl and A. Innes,[9] C. Beadle and H. Stevens,[10] F. Tiemann and C. Preusse,[11] J. Koenig and C. Krauch,[12] C.

---

[1] Ber. 1903, **36**, 2322; J. C. S. 1902, **84**, ii, 592; abst. Chem. Centr. 1904, II, 942.

[2] Zts. physik. Chem. 1902, **39**, 607; abst. J. C. S. 1902, **82**, ii, 248; Jahr. Chem. 1902, 205; Chem. Centr. 1902, I, 556.

[3] Zts. Phys. Chem. 1900, **33**, 129; abst. J. C. S. 1900, **78**, ii, 395.

[4] E. P. 10545, 1907; J. S. C. I. 1908, **27**, 558; C. A. 1909, **3**, 117.

[5] Papierfabr. **10**, 3; abst C. A. 1912, **6**, 2534.

[6] Zts. Farben. Ind. 1908, **7**, 236; abst. J. S. C. I. 1908, **37**, 851; C. A. 1910, **4**, 1384.

[7] Zts. ang. Chem. 1911, **24**, 1892; abst. J. S. C. I. 1911, **30**, 1247; Zts. Chem. Ind. Koll. 1912, **10**, 260.

[8] Monatsh. fur. tex. Ind. **26**, 155; Wag. Jahr. 1911, II, 417; Kunst. 1911, **1**, 401, 443; Chem. Ztg. Rep. 1912, **36**, 110; C. A. 1912, **6**, 2171.

[9] Zts. ang. Chem. 1910, **23**, 987; Wag. Jahr. 1910, II, 440; Chem. Ztg. 1910, **34**, 532; J. S. C. I. 1910, **29**, 687.

[10] C. N. 1913, **107**, 13; abst. C. A. 1913, **7**, 1284; Chem. Zentr. 1913, I, 970.

[11] Ber. 1879, **12**, 1768; abst. J. C. S. 1880, **38**, 137; Jahr. Chem. 1879, 1027.

[12] Zts. anal. Chem. 1880, **19**, 259; abst. Jahr. Chem. 1880, 1147; Chem. News, 1880, **42**, 206, 218. See also Ber. 1880, 154; Chem. News, 1880, **41**, 215.

Engler,[1] H. Herzog,[2] W. Manchot and J. Herzog,[3] Mohr,[4] C. Wicke,[5] W. Jorissen,[6] F. Haber and F. Bran,[7] S. Bigelow,[8] and by L. Meyer and F. Binnecker.[9]

Applications of the Cuprammonium Celluloses. Fremery and Urban, under the name of Pauly, in 1897 patented the first practical process for the manufacture of artificial filaments from cuprammonium cellulose solutions,[10] but inasmuch as ordinary cellulose dissolves but very slowly in Schweizer's reagent, and the solution is moreover accompanied by oxidation which modifies the cellulose molecule so that it is unfit for spinning purposes, the process was not a commercial success until Bronnert pro-

[1] Ber. 1900, **33**, 1102; abst. Jahr. Chem. 1900, 19; Chem Centr. 1900, I, 1153, 1154.

[2] Dissertation, Gött. 1901.

[3] Ann. 1901, **316**, 318; abst. Jahr. Chem. 1901, 1519; Chem. Centr. 1901, II, 350.

[4] Lehrb. anal. Titrirmeth. 1855, 271.

[5] Zts. für Chem. 1865, 89, 305; abst. Jahr. Chem. 1865, 265, 725; Chem. Centr. 1865, 493; Zts. anal. Chem. 1865, **4**, 424.

[6] Zts. phys. Chem. 1897, **23**, 667; abst. Jahr. Chem. 1897, 449; Chem. Centr. 1897, II, 724; Maandbl. Natuurw. **21**, 79.

[7] Zts. phys. Chem. 1900, **34**, 513; 1903, **35**, 81; abst. Jahr. Chem. 1900, 190; Chem. Centr. 1900, II, 936; 1901, I, 84.

[8] Zts. phys. Chem. 1898, **26**, 493; abst. J. C. S. 1898, **74**, ii, 506; Jahr. Chem. 1898, 246.

[9] Ber. 1887, **20**, 3058; abst. Jahr. Chem. 1887, 13. See also Kessler, Jahr. Chem. 1863, 124. Harcourt, Jahr. Chem. 1864, 9.

[10] U. S. P. 617009, 1899; abst. Mon. Sci. 1900, **56**, 6; 650715, 1900; abst. Rev. Chim. 1900, **3**, 32. 657818, 1900; 658632, 1900; abst. J. S. C. I. 1901, **20**, 38. 661214, 1900; 672350, 1901; abst. Mon. Sci. 1901, **57**, 283. 691257, 1902: abst. J. S. C. I. 1902, **21**, 272. 698254, 1902; abst. J. S. C. I. 1902, **21**, 705; Mon. Sci. 1902, **58**, 161. 705748, 1902; abst. J. S. C. I. 1902, **21**, 1150; Mon. Sci. 1903, **59**, 165. 804191, 1905; abst. J. S. C. I. 1905, **24**, 226, 1251; Mon. Sci. 1906, **65**, 69. 856857, 1907; abst. J. S. C. I. 1907, **26**, 836; C. A. 1907, **1**, 924; Mon. Sci. 1907, **67**, 159. E. P. 28631, 1897; 6557, 1899; abst. J. S. C. I. 1900, **19**, 239. 6641, 1899; abst. J. S. C. I. 1900, **19**, 240. 6656, 1899. 6735, 1899; abst. J. S. C. I. 1900, **19**, 344. 20630, 1899; abst. J. S. C. I. 1900, **19**, 821. 24101, 1899; abst. J. S. C. I. 1900, **19**, 1105; 1902, **21**, 1150; Rev. Chim. 1900, **2**, 34. 4303, 1900; abst. J. S. C. I. 1901, **20**, 1207. 20801, 1900; abst. J. S. C. I. 1901, **20**, 1231; J. Soc. Dyers Col. 1901, **17**, 295; Chem. Zts. 1901–1902, **1**, 580. F. P.: 286692, 1899; abst. Rev. Chim. 1900, **2**, 175; first addn. dated Oct. 14, 1899 to F. P. 286692, 1899; abst. Rev. Chim. 1900, **2**, 444. 286726, 1899; abst. Rev. Chim. 1900, **2**, 303; first addn. dated Dec. 4, 1899, to F. P. 86726, 1899. 286925, 1899; abst. Mon. Sci. 1899, **54**, 198; Rev. Chim. 1899, **1**, 441. D. R. P. 111313, 1899; abst. Chem. Centr. 1900, II, 550; Wag. Jahr. 1900, II, 448. 111409; abst. Wag. Jahr. 1900, II, 447; 111790, addn. to D. R. P. 111409. 121429, 1899; abst. Mon. Sci. 1901, **57**, 283. 121430, 1899; addn. to D. R. P. 121429, 1899; abst. Mon. Sci. 1901, **57**, 283. 271656, 1912; abst. C. A. 1914, **8**, 2813; Kunst. 1914, **4**, 193. Belg. P. 141697, 141721, 141756, 145510, 146487, 1899; 147579, 1900; 155637, 1901. Aust. P. 3636, 6843, 11879. Swiss P. 16077, 1898. Can. P. 60705, 1898. Ind. Text. **16**, 352.

posed the use of cellulose hydrate instead of cellulose as the initial cellulosic material, and thus laid the foundation for the cuprammonium silk industry of today.

Cuprammonium artificial filaments, known as "Glanzstoff," "Pauly Silk," "Cuprate Silk," "Kuproid," "Lustracellulose," "Soie de Hal," and "Parisian Silk," in the trade, are produced by forcing cuprammonium cellulose solutions, through glass or platinum spinnerets into a coagulating solution, washing out the reacting chemicals, and drying and otherwise treating the filaments thus formed. The processes for this purpose as patented by A. Lecoeur,[1] D. Lance,[2] A. Lacroix, J. Sella and J. de Sauverzac,[3] A. Kracht,[4] E. Knecht, A. Perl and P. Spence & Sons, Ltd.,[5] A. Hart,[6] R. Hömberg,[7] J. Hartogs,[8] Hanauer Kunstseiderfab-

[1] U. S. P. 863801, 1907. E. P. 8910, 1906; abst. J. S. C. I. 1906, **25**, 984. F. P. 362986, 365099, 1906; abst. J. S. C. I. 1906, **25**, 808, 925. D. R. P. 185294, 1906; abst. Wag. Jahr. 1907, II, 393; Chem. Ztg. Rep. 1907, **31**, 303; Zts. ang. Chem. 1907, **20**, 1542; Chem. Zentr. 1907, II, 1035. Aust. P. 30496. U. S. P. 863802, 1907. E. P. 16442, 1906; abst. J. S. C. I. 1907, **26**, 963. F. P. 374277, 1906; abst. J. S. C. I. 1907, **26**, 761; Mon. Sci. 1908, (4), **68**, 28. U. S. P. 967397, 1910. F. P. 381939, 1907; abst. J. S. C. I. 1908, **27**, 221. E. P. 18936, 1907; abst. J. S. C. I. 1908, **27**, 745; C. A. 1909, **3**, 380. U. S. P. 980294, 1911; C. A. 1911, **5**, 1188; Kunst. 1911, **1**, 174; J. S. C. I. 1911, **30**, 126. F. P. 410827, 1909; abst. J. S. C. I. 1910, **29**, 810; E. P. 22413, 1909. E. P. 14143, 1908; abst. C. A. 1910, **4**, 108. F. P. 392868, 1907; abst. J. S. C. I. 1909, **28**, 88; Mon. Sci. 1909, (4), **70**, 147. E. P. 21191, 1908; (Soc. anon. LeCrinoid). F. P. 392869, 1907; abst. J. S. C. I. 1909, **28**, 88. Belg. P. 189870, 1906.

[2] F. P. 435156, 1910; abst. J. S. C. I. 1912, **31**, 328. Belg. P. 234303, 1911. Compare Rheinische Kunstseidefabrik, Aust. Anm. A-9791, 1911. H. Heyderhaus, A. Banhegyi and K. Glaser, F. P. 406139, 1909; abst. J. S. C. I. 1910, **29**, 417. P. Minck, U. S. P. 1317306; abst. C. A. 1919, **13**, 3316.

[3] F. P. 402125, 1908; abst. Mon. Sci. 1910, (4), **24**, 290.

[4] F. P. 355064, 1905; abst. J. S. C. I. 1905, **24**, 1226; Mon. Sci. 1906, **65**, 167. Belg. P. 183521, 1905.

[5] E. P. 25532, 1911; abst. J. S. C. I. 1913, **32**, 18; C. A. 1913, **7**, 1608; Kunst. 1913, **3**, 73. F. P. 449801, 1912; abst. J. S. C. I. 1913, **32**, 483. E. P. 25533, 1911; abst. J. S. C. I. 1913, **32**, 18; C. A. 1913, **7**, 1608; Kunst. 1913, **3**, 73. F. P. 449803, 1912; abst. J. S. C. I. 1913, **32**, 483. E. P. 25534, 1911; abst. J. S. C. I. 1913, **32**, 19; C. A. 1913, **7**, 1608; Kunst. 1913, **3**, 74. F. P. 449802, 1912; abst. J. S. C. I. 1913, **32**, 483.

[6] E. P. 18607, 1910; J. S. C. I. 1911, **30**, 1448. F. P. 433013, 1911; J. S. C. I. 1912, **31**, 123; Mon. Sci. 1913, **78**, 24. See E. Crumiere, U. S. P. 904684. Belg. P. 194941, 1906; 205672, 206788, 1908. D. R. P. 201915, 1908; abst. Chem. Ztg. 1909, **33**, 66; Zts. Chem. Ind. Koll. 1908, **3**, 245.

[7] U. S. P. 983139, 1911; J. S. C. I. 1911, **30**, 278. D. R. P. Anm. H-51313, 1910. D. R. P. 235366, 1910; C. A. 1911, **5**, 3169; J. S. C. I. 1911, **30**, 1248; Zts. ang. Chem. 1911, **24**, 1499; Chem. Zentr. 1911, II, 175; Wag. Jahr. 1911, II, 418; Kunst. 1911, **1**, 275. D. R. P. 237717, 1909; J. S. C. I. 1911, **30**, 1248; C. A. 1912, **6**, 1679; Zts. ang. Chem. 1911, **24**, 1988; Chem. Zentr. 1911, II, 922; Wag. Jahr. 1911, II, 418; Kunst. 1911, **1**, 378. Belg. P. 227722, 1910.

[8] U. S. P. 1119155, 1914; abst. C. A. 1915, **9**, 247; J. S. C. I. 1915,

rik,[1] G. Guadagni,[2] Glanzfaden Akt. Ges.,[3] R. Frericks,[4] and also F.

34, 25. D. R. P. 237744, 1910; abst. J. S. C. I. 1911, **30,** 1249; Chem. Zentr. 1911, II, 814; Wag. Jahr. 1911, II, 423.

[1] U. S. P. 839825, 1907; J. S. C. I. 1907, **26,** 340; C. A. 1907, **1,** 791. U. S. P. 840611, 1907; J. S. C. I. 1907, **26,** 340; C. A. 1907, **1,** 792. E. P. 10164, 1907; J. S. C. I. 1907, **26,** 1026; C. A. 1907, **1,** 2651. E. P. 10165, 1907; J. S. C. I. 1907, **26,** 888. F. P. 377325, 1907; J. S. C. I. 1907, **26,** 1026. F. P. 377326, 1907; J. S. C. I. 1907, **26,** 1004; Mon. Sci. 1908, (4), **68,** 29. D. R. P. 187696, 1906; Chem. Zentr. 1907, II, 1768; Jahr. Chem. 1905–1908, 988; Chem. Tech. Rep. 1907, **31,** 449; Chem. Ind. 1907, **30,** 451; Wag. Jahr. 1907, II, 392; Mon. Sci. 1910, (4), **72,** 76. D. R. P. 220711, 1909; 221041, 1908; C. A. 1910, **4,** 2732; J. S. C. I. 1910, **29,** 689; Chem. Zentr. 1910, I, 1662; Jahr. Chem. 1910, 427; Wag. Jahr. 1910, II, 429. D. R. P. 222873, 1908; Jahr. Chem. 1910, 427. D. R. P. 222893, 1908; addn. to D. R. P. 221041, 1908; J. S. C. I. 1910, **29,** 875. D. R. P. 231693, 1906; C. A. 1911, **5,** 2737; J. S. C. I. 1911, **30,** 484; Chem. Zentr. 1911, I, 770; Wag. Jahr. 1911, II, 416; Kunst. 1911, **1,** 114. D. R. P. 232873, Wag. Jahr. 1910, II, 430; C. A. 1911, **5,** 2737, 3157. D. R. P. 233370, 1908; C. A. 1912, **6,** 1854. D. R. P. 235219, 1909; C. A. 1911, **5,** 3157; J. S. C. I. 1911, **30,** 484; Zts. ang. Chem. 1911, **24,** 1341; Chem. Zentr. 1911, II, 119; Wag. Jahr. 1911, II, 416; Kunst. 1911, **1,** 275. D. R. P. 240242, 1908; C. A. 1912, **6,** 2169; J. S. C. I. 1911, **30,** 1447; Zts. Chem. Ind. Koll. 1912, **10,** 62; Zts. ang. Chem. 1911, **24,** 2334; Chem. Zentr. 1911, II, 1567; Wag. Jahr. 1911, II, 417; Kunst. 1911, **1,** 456. D. R. P. 255549, 1911; C. A. 1913, **7,** 1811; J. S. C. I. 1913, **32,** 420; Kunst. 1913, **3,** 20, 53. D. R. P. 260650, 1908; C. A. 1913, **7,** 3237; J. S. C. I. 1913, **32,** 748. Aust. P. 50506, 1909; Kunst. 1912, **2,** 75. Belg. P. 199881, 199882, 1907.

[2] U. S. P. 977863, 1910; J. S. C. I. 1911, **30,** 19; C. A. 1911, **5,** 994. U. S. P. 978878, 1910; C. A. 1911, **5,** 995. U. S. P. 979013, 1910. E. P. 1265, 1908; J. S. C. I. 1908, **27,** 682. E. P. 25986, 1910; C. A. 1912, **6,** 161; J. S. C. I. 1911, **30,** 1050; Kunst. 1911, **1,** 416. F. P. 386339, 1908; J. S. C. I. 1908, **27,** 682. D. R. P. 216669, Chem. Zentr. 1910, I, 217; Jahr. Chem. 1910, 426; Chem. Tech. Rep. 1910, **34,** 23; Chem. Ind. 1909, **32,** 837; Wag. Jahr. 1909, II, 394. Aust. P. 51799, Kunst. 1912, **2,** 156. Belg. P. 205243, 1908. Swiss P. 42305, 1908.

[3] D. R. P. 228872, 1908; abst. C. A. 1911, **5,** 2177; Zts. ang. Chem. 1911, **24,** 1151; Chem. Zentr. 1911, I, 51; Kunst. 1911, **1,** 34. D. R. P. 230141, 237716, 241921, being addn. to D. R. P. 228872. Aust. P. 46861. F. P. 400321 (F. Friedrich). Swiss P. 45764. E. P. 4104, 1909. U. S. P. 945559 (R. Linkmeyer). D. R. P. 230141, 1908; addn. to D. R. P. 228872, 1908; abst. C. A. 1911, **5,** 2732; J. S. C. I. 1911, **30,** 1248; Zts. ang. Chem. 1911, **24,** 286; Chem. Zentr. 1911, I, 364; Wag. Jahr. 1911, II, 414; Kunst. 1911, **1,** 74. D. R. P. 237716, 241921; addn. thereto. F. P. 10732, addn. to F. P. 400321 (P. Friedrich). E. P. 7617, 1909. Swiss P. 48576. U. S. P. 979013 (R. Linkmeyer). Aust. P. 47147 (P. Friedrich). D. R. P. 237716, 1908; addn. to D. R. P. 228872, 1908; abst. C. A. 1912, **6,** 1679; J. S. C. I. 1911, **30,** 1248; Zts. ang. Chem. 1911, **24,** 1988; Chem. Zentr. 1911, II, 922; Kunst. 1911, **1,** 378. U. S. P. 962770. F. P. 404372. E. P. 14112, 1909 (R. Linkmeyer). Swiss P. 48679 (P. Friedrich). D. R. P. 241683, 1909; abst. C. A. 1912, **6,** 2170; J. S. C. I. 1912, **31,** Zts. ang. Chem. 1912, **25,** 286; Wag. Jahr. 1911, II, 418; Kunst. 1912, **2,** 57. D. R. P. 241921, 1909; addn. to D. R. P. 228872; abst. C. A. 1912, **6,** 2181; Zts. ang. Chem. 1912, **25,** 286. D. R. P. 269787, 1908; abst. C. A. 1914, **8,** 2251; Kunst. 1914, **4,** 40, 96. D. R. P. 286297, 1913; abst. C. A. 1916, **10,** 1101; J. S. C. I. 1916, **35,** 173. D. R. P. Anm. 26613, 1908; 26679; abst. Kunst. 1913, **3,** 140. F-28001, 28869, 1909. G-39779, 1913; abst. Kunst. 1914, **4,** 384.

[4] U. S. P. 729749, 1903; abst. Mon. Sci. 1903, **59,** 165. D. R. P. 137461; abst. Wag. Jahr. 1903, II, 415; Chem. Zts. 1902–1903, **2,** 438. Ac-

G. Donnersmarck'sche Kunsteiden und Acetatwerke,[1] W. Dreaper,[2] G. Ditzler,[3] R. Adler,[4] J. Boullier and J. Lafais,[5] G. Boucquey,[6] H. Bernstein,[7] A. Pellerin,[8] R. Pawlikowski,[9] Palatine Artificial Silk Yarn Co., Ltd.,[10] Rheinische Kunstseide Fabrik,[11]

---

cording to E. Rasser (Papier Fabr. 1918, **16**, 621, 645; C. A. 1919, **13**, 1926, 2277) textile papers and yarn may be waterproofed by impregnation with a solution of parchment clippings in cuprammonium hydroxide, followed by removal of the copper and formation of a basic aluminum sulfate on the fibers by means of an aluminum soap.

[1] F. P. 398424, 1909. D. R. P. 212594; abst. Chem. Zentr. 1909, II, 774; Wag. Jahr. 1909, II, 203. E. P. 1407, 1909; abst. J. S. C. I. 1910, **29**, 208. Swiss P. 47395.

[2] E. P. 27222, 1905. Belg. P. 196857, 1906. F. P. 373088, 1906. E. P. 11959, 1908; J. S. C. I. 1909, **28**, 791. E. P. 20316, 1908; J. S. C. I. 1909, **28**, 121; J. Soc. Dyers Col. 1909, **25**, 314; C. A. 1910, **4**, 827. Belg. P. 196857, 1906.

[3] D. R. P. 244510, 1911; C. A. 1912, **6**, 2327; Zts. ang. Chem. 1912, **25**, 1034; Wag. Jahr. 1912, II, 439; Kunst. 1912, **2**, 100. E. P. 9336, 1911; abst. C. A. 1912, **6**, 3019; J. S. C. I. 1912, **31**, 180; J. Soc. Dyers Col. 1912, **28**, 120; Kunst. 1912, **2**, 134. Belg. P. 225041, 226352, 1910.

[4] U. S. P. 1169756, 1916; abst. C. A. 1916, **10**, 973; J. S. C. I. 1916, **35**, 303; Mon. Sci. 1916, **83**, 78.

[5] J. Boullier and J. Lafais, E. P. 16512, 1907; 15015, 1908. F. P. 392442, 1908; J. S. C. I. 1908, **27**, 1201.

[6] F. P. 368706, 1906; J. S. C. I. 1907, **26**, 17. F. P. 376065, 1907; Mon. Sci. 1908, **68**, 87. Belg. P. 186233, 1905; 191080, 1906.

[7] U. S. P. 798868, 1905; 960791, 1910; J. S. C. I. 1910, **29**, 810; C. A. 1910, **4**, 2574. U. S. P. 965273, 1910; C. A. 1910, **4**, 2732; J. S. C. I. 1910, **29**, 1105. U. S. P. 965557, 1910; J. S. C. I. 1910, **29**, 1105. E. P. 849, 1911. E. P. 15991, 1910; C. A. 1911, **5**, 3622; J. S. C. I. 1911, **30**, 957. F. P. 418282, 1910; Mon. Sci. 1913, **78**, 86. D. R. P. Anm. B-59472, 1910. D. R. P. 248303, 1910; Kunst. 1912, **2**, 240, 295; Zts. ang. Chem. 1912, **25**, 1804; C. A. 1912, **6**, 3019; Wag. Jahr. 1912, II, 440. D. R. P. 254029, 1905; J. S. C. I. 1905, **24**, 1011. Swiss P. 53440, 1910; Kunst. 1912, **2**, 156. Can. P. 100206, 1906. Belg. P. 227339, 1910.

[8] Belg. P. 255192; abst. Kunst. 1914, **4**, 16. Swiss P. 64190, 1913; abst. C. A. 1914, **8**, 2482. D. R. P. 271215; abst. C. A. 1914, **8**, 2491.

[9] E. P. 16629, 1910; abst. J. S. C. I. 1911, **30**, 1009; C. A. 1911, **5**, 3919. F. P. 417851, 1910; abst. Kunst. 1911, **1**, 196. D. R. P. 235325, 1910; abst. Chem. Zentr. 1911, II, 119; C. A. 1911, **5**, 3169. E. P. 17089, 1910; abst. J. S. C. I. 1911, **30**, 1052. F. P. 403488, 1909; abst. Mon. Sci. 1910, **73**, 169; C. A. 1911, **5**, 1514. D. R. P. 222624, 1908; abst. C. A. 1910, **4**, 3004; Wag. Jahr. 1910, II, 260; Jahr. Chem. 1910, 427. Aust. P. 49170; abst. Kunst. 1911, **1**, 378. Swiss P. 49399. F. P. 431074, 1911; abst. J. S. C. I. 1911, **30**, 1375; Kunst. 1912, **2**, 17. D. R. P. 237200, 1909; abst. C. A. 1912, **6**, 1536; Chem. Zentr. 1911, II, 500; Kunst. 1911, **1**, 339. D. R. P. 237240, 1909. D. R. P. 248172, 1910; abst. Zts. ang. Chem. 1912, **25**, 1548; Kunst. 1912, **2**, 254; C. A. 1912, **6**, 3019; Wag. Jahr. 1912, II, 440. D. R. P. Applications P-24172, 1909; P-25543, 25760, 26509, 1910; V-4289, 1909. Belg. P. 216341, 216546, 1909; 236204, 1911. Swiss P. 49399, 1909. Aust. P. Application A-4926, 1911.

[10] E. P. 9336, 1911; abst. C. A. 1912, **6**, 3019; J. S. C. I. 1912, **31**, 183; J. Soc. Dyers Col. 1912, **28**, 120; Kunst. 1912, **2**, 134.

[11] F. P. 405571; abst. J. S. C. I. 1910, **29**, 417. D. R. P. 231652, 1909; abst. C. A. 1911, **5**, 2737; Chem. Zentr. 1911, I, 770; Wag. Jahr. 1911, II, 415. D. R. P. 236537, 1908; abst. C. A. 1912, **6**, 1231; Chem. Zentr.

Soc. anon. la Soie nouvelle,[1] Soc. la Soie Artificielle de Nord,[2] E. Thiele and Soc. Gen. de la Soie Artificielle Linkmeyer,[3] Ver. Kunstseidefabriken,[4] J. Vermeesch,[5] Consortium Mulhousien pour la fabrication de fils,[6] Farb. vorm. Meister, Lucius and Brüning,[7]

1911, II, 326; Wag. Jahr. 1911, II, 415. D. R. P. 237816, 1910; abst. C. A. 1912, **6**, 1679; Chem. Zentr. 1911, II, 1085; Wag. Jahr. 1911, II, 416. E. P. 18342, 1909; abst. J. S. C. I. 1910, **29**, 557.

1. F. P. 365057, 1906; abst. C. A. 1907, **1**, 2429; J. S. C. I. 1906, **25**, 1041. U. S. P. 836620. E. P. 9254, 1906; abst. J. S. C. I. 1907, **26**, 91, 252 (J. Vermeesch).

2. F. P. 379000, 1906; abst. J. S. C. I. 1907, **26**, 1196. F. P. 385053, 1907; abst. Mon. Sci. 1908, (4), **68**, 166; same as D. R. P. of Apr. 27, 1907. F. P. 442019. Belg. P. 244554, 1912.

3. E. P. 15133, 1906; abst. J. S. C. I. 1906, **25**, 1040. F. P. 367979; abst. J. S. C. I. 1906, **25**, 1144. U. S. P. 909257 (E. Thiele); abst. J. S. C. I. 1909, **28**, 137. E. P. 16088, 1906; abst. J. S. C. I. 1907, **26**, 45. D. R. P. 179772; abst. Wag. Jahr. 1906, II, 392; C. A. 1907, **1**, 2202; Zts. ang. Chem. 1907, **20**, 461; Chem. Zentr. 1907, I, 1472; Chem. Tech. Rep. 1907, **31**, 37. F. P. 357837. Aust. P. 35264. E. Thiele, Belg. P. 171980, 1903; 192856, 1906. Soc. Gen. de la Soie Artificielle Linkmeyer, Belg. P. 185875, 188519, 1905. See also R. Linkmeyer, Belg. P. 181360, 1904; 181944, 183945, 183603, 186898, 1905. E. Thiele, U. S. P. 710819; abst. J. S. C. I. 1902, **21**, 1393. E. P. 8083, 1902; abst. J. S. C. I. 1903, **22**, 550. F. P. 320446, 1902; abst. J. S. C. I. 1903, **22**, 25. D. R. P. 154507; abst. Wag. Jahr. 1904, II, 392; 1906, II, 391. D. R. P. 157157; addn. to D. R. P. 154507; abst. Wag. Jahr. 1904, II, 507. D. R. P. 173628, addn. to D. R. P. 154507; abst. C. A. 1907, **1**, 673; Chem. Centr. 1905, I, 576, 1906, II, 900; Jahr. Chem. 1905–1908, 987; Mon. Sci. 1908, (4), **68**, 160; Zts. ang. Chem. 1910, 987. Aust. P. 21119. D. R. P. 225161; addn. to D. R. P. 154507; abst. Wag. Jahr. 1910, II, 431; Chem. Zentr. 1910, II, 1010; Kunst. 1911, **1**, 16; Jahr. Chem. 1910, 427; U. S. P. 909257, 1909; abst. J. S. C. I. 1909, **28**, 137; C. A. 1909, **3**, 1090. E. P. 15133, 1906 (E. Thiele and Soc. Gen. Art. Linkmeyer); abst. J. S. C. I. 1906, **25**, 1040. F. P. 367979. Aust. P. 37119. Belg. P. 192856, 1906; 254161; abst. Kunst. 1913, **3**, 357. Rev. Prod. Chim. (21), **3**, 325; abst. J. S. C. I. 1901, **20**, 119. Zts. Farben, 1902, 73; abst. Wag. Jahr. 1902, II, 470.

4. D. R. P. 184510; abst. C. A. 1908, **2**, 347; Chem. Zentr. 1907, II, 1035; Chem. Tech. Rep. 1907, **31**, 257; Wag. Jahr. 1907, II, 391. D. R. P. 230941, 1908; abst. J. S. C. I. 1911, **30**, 484; C. A. 1911, **5**, 2736; Zts. ang. Chem. 1911, **24**, 479; Chem. Zentr. 1911, I, 697; Wag. Jahr. 1911, II, 941; Kunst. 1911, **1**, 91, 114. U. S. P. 986017 (F. Lehner). Aust. P. 57698; abst. Kunst. 1913, **3**, 178. Belg. P. 164907, 164908, 1902.

5. U. S. P. 836620, 1906; abst. J. S. C. I. 1907, **26**, 91; C. A. 1907, **1**, 503. E. P. 9254, 1906; abst. C. A. 1907, **1**, 1490; J. S. C. I. 1907, **26**, 252. F. P. 365057 (Soc. Anon. La Soie. Nouvelle.). U. S. P. 850695, 1907; abst. J. S. C. I. 1907, **26**, 527; C. A. 1907, **1**, 1787. F. P. 369973, 1906; abst. J. S. C. I. 1907, **26**, 319. E. P. 20408, 1906. Belg. P. 190509, 1906; 195684, 1906 (J. Vermeesch and F. Scheys). Belg. P. 188529, 1905 (J. Vermeesch and H. Monge).

6. F. P. 290405, 290406, 1899; abst. Mon. Sci. 1900, **56**, 125. Belg. P. 143569, 143570, 145201, 1899. E. P. 13331, 1899; abst. J. S. C. I. 1900, **19**, 531.

7. U. S. P. 779175, 1905; abst. J. S. C. I. 1905, **24**, 129. E. P. 21988, 1904; abst. J. S. C. I. 1905, **24**, 1010. F. P. 350220, 1905. D. R. P. 186387; abst. Jahr. Chem. 1905–1908, 989; Chem. Zentr. 1907, II, 1134, 1815; Wag. Jahr. 1907, 391; Chem. Tech. Rep. 1907, **31**, 361. Aust. P. 28151. D. R. P.190217, addn. to D. R. P. 186387. Belg. P. 180370, 1914.

H. Luxburg,[1] J. Hermans,[2] R. Müller,[3] J. Bemberg,[4] J. Foltzer and J. Vermeesch,[5] Le Crinoid Soc. Anon.,[6] F. Lehner,[7] K. Mueller, J. Schwarz and M. Scheid,[8] C. Muellet,[9] C. Mueller and D. Wolf,[10] Vereinigte Glanzstoff Fabriken,[11] E. Bron-

[1] E. P. 1407, 1909. F. P. 398424, 1909; abst. J. S. C. I. 1909, **28**, 880; 1910, **29**, 208.

[2] U. S. P. 1034235, 1912; C. A. 1912, **6**, 3018; J. S. C. I. 1912, **31**, 811; Mon. Sci. 1913, **78**, 110; Kunst. 1913, **3**, 16. E. P. 4610, 1912; J. S. C. I. 1912, **31**, 1075. F. P. 440907, 1907; J. S. C. I. 1912, **31**, 812.

[3] U. S. P. 779175, 1905; abst. J. S. C. I. 1905, **24**, 129; Chem. Zts. 1905, **4**, 89, 540.

[4] D. R. P. 162866, 1900; Jahr. Chem. 1905–1908, 987; Wag. Jahr. 1905, II, 393; J. S. C. I. 1906, **25**, 38. D. R. P. 174508, 1905, addn. to D. R. P. 162866, 1900; Wag. Jahr. 1906, II, 386; C. A. 1907, **1**, 951; Mon. Sci. 1908, (4), **68**, 160.

[5] Belg. P. 181525, 1906.

[6] U. S. P. 980294, 1911. E. P. 22413, 1909; abst. J. S. C. I. 1910, **29**, 1053; C. A. 1911, **5**, 2429; Kunst. 1911, **1**, 34. F. P. 410827, 1909; abst. J. S. C. I. 1910, **29**, 810. Belg. P. 217312, 1909.

[7] Belg. P. 153296, 1900.

[8] E. P. 3725, 1890; abst. J. S. C. I. 1891, **10**, 539.

[9] F. P. 373429, 1907; abst. Mon. Sci. 1908, (4), **68**, 83; J. S. C. I. 1907, **26**, 713.

[10] E. P. 5659, 1912. F. P. 443133, 1912; abst. J. S. C. I. 1912, **31**, 1029; 1913, **32**, 133.

[11] Verein. Glanzstoff-Fabriken, A. G., E. P. 1283, 1905; abst. J. S. C. I. 1905, **24**, 1251. U. S. P. 806533. F. P. 351208, 1905; abst. J. S. C. I. 1905, **24**, 856. D. R. P. 169567; abst. Wag. Jahr. 1906, II, 385; J. S. C. I. 1906, **25**, 775; Mon. Sci. 1908, (4), **68**, 45. See also F. P. 351206, 1905. E. P. 1284, 1905; abst. J. S. C. I. 1905, **24**, 1106. F. P. 351206, 1909; abst. J. S. C. I. 1905, **24**, 855. U. S. P. 856857. D. R. P. 186766, 1904; abst. Mon. Sci. 1910, (4), **72**, 76; Zts. ang. Chem. 1908, **21**, 271; Chem. Zentr. 1907, II, 1767; Chem. Tech. Rep. 1907, **31**, 395; Chem. Ind. 1907, **30**, 413; Wag. Jahr. 1907, 390. See also E. P. 1745, 1905; abst. J. S. C. I. 1905, **24**, 1320. F. P. 351207, 351208, 1905; abst. J. S. C. I. 1905, **24**, 856; Mat. Col. 1905, **9**, 503. U. S. P. 804191. Aust. P. 32377. D. R. P. 186766, 1904; abst. Chem. Tech. Rep. 1907, **31**, 395; Wag. Jahr. 1907, 390; Chem. Zentr. 1907, II, 1767. D. R. P. 188113, 1905, addn. to D. R. P. 186766, 1904; abst. Mon. Sci. 1910, (4), **72**, 76; Chem. Zentr. 1907, II, 1768; Chem. Tech. Rep. 1907, **31**, 504; Wag. Jahr 1907, 390. E. P. 16495, 1907; abst. J. S. C. I. 1907, **26**, 1004. F. P. 379935. 1907; abst. J. S. C. I. 1907, **26**, 1237. D. R. P. 235134, 1906; abst. Kunsf, 1911, **1**, 255; Zts. ang. Chem. 1911, **24**, 1340; Chem. Zentr. 1911, II, 64. Aust. P. 35269. Swiss P. 41109, 1907. See also D. R. P. 259816, 1910; abst. C. A. 1913, **7**, 3227; Kunst. 1913, **3**, 196. E. P. 18936, 1907. E. P. 22092, 1907. Aust. P. 35272. E. P. 27707, 1907; abst. J. Soc. Dyers. Col. 1909, **25**, 17. D. R. P. 208472, 1907; abst. C. A. 1909, **3**, 2052; Chem. Zentr. 1909, I, 1370; Chem. Ztg. Rep. 1909, 216; Chem. Tech. Rep. 1909, **32**, 216; Chem. Ind. 1909, **32**, 211; Wag. Jahr. 1909, II, 392; Chem. Zts. 1909, **8**, 1395. D. R. P. 218490, addn. to D. R. P. 208472; abst. C. A. 1910, **4**, 2044; Chem. Zentr. 1910, I, 784; Jahr. Chem. 1910, 426; Chem. Tech. Rep. 1910, **34**, 135; Chem. Ind. 1910, **33**, 154; Wag. Jahr. 1910, II, 427; Chem. Zts. 1910, **9**, 1836. D. R. P. 229863, addn. to D. R. P. 208472. Aust. P. 35275. F. P. 9253, addn. to F. P. 385083 (Soc. Anon. La Soie Artificielle). Swiss P. 41554, 1907. E. P. 9268, 1908; abst. J. S. C. I. 1908, **27**, 897. D. R. P. 229863, addn. to D. R. P. 208472; abst. C. A. 1911, **5**, 2723; Ztg. ang. Chem. 1911, **24**, 285; Chem. Zentr. 1911, I, 364; Wag. Jahr.

nert,[1] and others,[2] are among the numerous investigators whose results are described in detail in Volume IV of this present series.

1911, II, 414; Kunst. 1911, **1**, 74. Aust. P. 35275. F. P. 385083 (Soc. anon. La Soie Aritficielle). E. P. 309, 1911; abst. J. S. C. I. 1911, **30**, 484. U. S. P. 1055513; abst. J. S. C. I. 1913, **32**, 422. F. P. 424621, 1911. E. P. 15700, 1910; abst. Kunst. 1911, **1**, 75. E. P. 27539, 1910; abst. J. S. C. I. 1911, **30**, 415. F. P. 423064. D. R. P. 239214; abst. C. A. 1912, **6**, 2169; Zts. ang. Chem. 1911, **24**, 2229; Wag. Jahr. 1911, 419; Kunst. 1911, **1**, 456. E. P. 27600, 1910; abst. J. S. C. I. 1911, **30**, 616. U. S. P. 1049201; abst. J. S. C. I. 1913, **32**, 133. F. P. 423104; abst. J. S. C. I. 1911, **30**, 615. D. R. P. 235476; abst. Zts. ang. Chem. 1911, **24**, 1499; Chem. Zentr. 1911, II, 175. E. P. 29046, 1910; abst. J. S. C. I. 1911, **30**, 1051; C. A. 1912, **6**, 1526. F. P. 424419, 1910; abst. J. S. C. I. 1911, **30**, 740. E. P. 29246, 1910; abst. J. S. C. I. 1911, **30**, 888. F. P. 423774, 1910; abst. J. S. C. I. 1911, **30**, 615. E. P. 2992, 4922, 1913; abst. J. S. C. I. 1914, **33**, 72; C. A. 1914, **8**, 2805. F. P. 454811, 1913; abst. J. S. C. I. 1913, **32**, 865; Mon. Sci. 1914, 43; C. A. 1914, **8**, 572; Kunst. 1913, **3**, 356. U. S. P. 1106077; abst. J. S. C. I. 1914, **33**, 859. D. R. P. 268261, 1912; abst. C. A. 1914, **8**, 1668; Kunst. 1913, **3**, 459. F. P. 426089, 434621, 1911. D. R. P. 190217, addn. to D. R. P. 186257. (Meister, Lucius and Bruening); abst. Chem. Zentr. 1907, II, 1815; Jahr. Chem. 1905–1908, 989; Wag. Jahr. 1907, 392. D. R. P. 231279, 1910. D. R. P. 236584, 1910; abst. Kunst. 1911, **1**, 277; 1912, **2**, 75. D. R. P. 240846, 1908; abst. C. A. 1912, **6**, 2169; J. S. C. I. 1912, **31**, 67; Zts. ang. Chem. 1912; **25**, 47; Chem. Zentr. 1911, II, 843; Wag. Jahr. 1911, II, 421; Text. Col. 1912, **34**, 71; Kunst. 1912, **2**, 15. D. R. P. 274550, 1914; abst. C. A. 1915, **9**, 2590, F. P. 454011, 1913; abst. C. A. 1914, **8**, 257. D. R. P. 283286, 1913; abst. Kunst. 1915, **5**, 72. D. R. P. Anm. V-9306, 9387, 9388, 1910; V-9635, 1910. abst. Kunst. 1912, **2**, 379; V-10780, 1912; abst. Kunst. 1914, **4**, 100. Aust. P. 54819; abst. Kunst. 1912, **2**, 456. Aust. Anm. A-115, 1911; abst. Kunst. 1912, **2**, 320; A-756, 1905; abst. Mon. Sci. 1910, (4), **72**, 45; A-1677, 1913; abst. Kunst. 1914, **4**, 260; A-5148, 1910; A-9230, 9285, 1910. Belg. P. 182368, 182455, 182486, 1905; 203012, 1907; 204557, 1907. D. R. P. 208472, 1907. Belg. P. 243387, 1910; 254219; abst. Kunst. 1913, **3**, 356. Can. P. 120762, 1909. Hung. Anm. G-3210, 3227, 1911. Swed. P. 40463, 1916; abst. C. A. 1916, **9**, 2044. Swiss P. 53936, 1910. Kunst. 1912, **2**, 100, 158, 178, 196; 1913, **3**, 78, 197; 1914, **4**, 137; 1915, **5**, 83; Chem. Ztg. 1911, 1186.

1. E. Bronnert, U. S. P. 646351; abst. Mon. Sci. 1900, **56**, 219. 646381; abst. Mon. Sci. 1900, **56**, 218; Rev. Chim. 1900, **2**, 304. 646799, abst. Mon. Sci. 1900, **56**, 219; Rev. Chim. 1900, **2**, 351. 1023548, 1912; J. S. C. I. 1912, **31**, 485; C. A. 1912, **6**, 1672; 1049201, 1912; C. A. 1913, **7**, 700; J. S. C. I. 1913, **32**, 133; 1055513, 1913; C. A. 1913, **7**, 1608; J. S. C. I. 1913, **32**, 422; 1102237, 1914; C. A. 1914, **8**, 2947; J. S. C. I. 1914, 828; 1106077, 1914; C. A. 1914, **8**, 3237; J. S. C. I. 1914, **33**, 859. E. P. 13331, 1899; 18260, 1899; abst. J. S. C. I. 1900, **19**, 659; 18884, 1899; abst. J. S. C. I. 1900, **19**, 531; 22092, 1907; abst. J. S. C. I. 1907, **26**, 1275; J. Soc. Dyers Col. 1908, **24**, 118; 27539, 1910; J. S. C. I. 1911, **30**, 415; E. P. 309, 1911; J. S. C. I. 1911, **32**, 484. F. P. 278371; 292988, abst. Mon. Sci. 1900, **56**, 224; 423104, 1910; J. S. C. I. 1911, **30**, 615; 454811, 1913; J. S. C. I. 1913, **32**, 865. D. R. P. 109996, 1899; Jahr. Chem. 1900, 843; Wag. Jahr. 1900, II, 448; Mon. Sci. 1901, (4), **57**, 20. 111313, 1899; 118836, 1899; Jahr. Chem. 1901, 890; Wag. Jahr. 1901; II, 514; Mon. Sci. 1901, (4), **57**, 213; 118837, addn. to D. R. P. 118836, 1899; Jahr. Chem. 1901, 890; Wag. Jahr. 1901, II, 514; Mon. Sci. 1901, (4), **57**, 213. Aust. P. 3638, 11066. Belg. P. 143569, 1899; Bull. soc. Ind. Mulhouse, 1900, 177; Chem. Centr. 1900, II, 749; Jahr. Chem. 1900, 843; Mon. Text. Ind. 1901, **16**, 817. E. Bronnert and M. Fremery, U. S. P. 1030251, 1912; J. S. C. I. 1912, **31**, 680; Kunst. 1912, **2**, 457. E. P. 22092, 1907; 9268, 1908; J. S. C. I. 1908, **27**, 897. E. Bronnert, M. Fremery and J. Urbain, U. S. P.: 617009, 658632, 1900. 672350, 1901;

Cellulose and Hydrochloric Acid. It has for some time been known that concentrated hydrochloric acid exerts a dissolving influence upon cellulose and that cellulose does not withstand the action of fuming hydrochloric acid for any length of time, but breaks down by the rupture of the fibers into a pulp that is

Mon. Sci. 1901, (4), **57**, 283; 698254, 1902; J. S. C. I. 1902, **21**, 706; Mon. Sci. 1902, **58**, 161; 691257, 764943, 764944; Mon. Sci. 1905, **62**, 16. E. P. 28631, 1897; 13300, 1899. 1763, 1900; J. S. C. I. 1901, **20**, 119; 4303, 1900; J. S. C. I. 1901, **20**, 1207. 20801, 1900; J. S. C. I. 1901, **20**, 1231; 4303, 1901. F. P. 272718, 292988, 308715, 1901; J. S. C. I. 1902, **21**, 49; Mon. Sci. 1902, (4), **58**, 37. D. R. P. 98642, Jahr. Chem. 1898, 1370; Wag. Jahr. 1903, II, 417. 115989; Wag. Jahr. 1900, II, 446. 119098, 1899; Jahr. Chem. 1901, 890; Mon. Sci. 1901, (4), **57**, 213. 119099, addn. to D. R. P. 119098; Jahr. Chem. 1901, 891; Mon. Sci. 1901, (4), **57**, 213. 119230, 1900; Mon. Sci. 1901, 900; Mon. Sci. 1901, (4), **57**, 213; 125310; Wag. Jahr. 1901, II, 513; Mon. Sci. 1902, (4), **58**, 130. Aust. 6150, 6064, 8596, 10263, 11066. Belg. P. 147579, 1900. Can. P. 81298, 1903; 99425, 1906. E. Bronnert and T. Schlumberger, E. P. 6858, 1898.

2. Grandquist, D. R. P. 111248, 111333; Wag. Jahr. 1903, II, 417. G. Hager, D. R. P. 163233, 1904. A. Helbronner and E. Vallee, D. R. P. 197250; abst. Mon. Sci. 1911, 53. F. P. 361796. Swiss P. 41005. Chem. Fabr. von Heyden, A. G., Belg. 232475, 1911. P. Joliot, F. P. 468337, 1913. L. Leduc, H. Jaquemin and Soc. Anon. des Soieries de Maransart, Belg. P. 253537; abst. Kunst. 1913, **3**, 356. W. Bruckner, D. R. P. 241781, 1909; addn. to D. R. P. 238361, 1909; abst. J. S. C. I. 1912, **31**, 227. Rheinische Kunstseide Fabrik Akt. Ges. E. P. 18342, 1909. F. P. 405571, 1909; J. S. C. I. 1910, **29**, 417. D. R. P. 231652, 236817, 236537, 237816; J. S. C. I. 1911, **30**, 1248. E. Crumiere, U. S. P. 908754, 911868, 1909. Compagnie Francaise des Applications de la Cellulose, Swiss P. 57951. Aust. Anm. 4369, 1911. O. Dony-Henault, Eighth Inter. Cong. Appl. Chem. 1912, **2**, 83; C. A. 1912, **6**, 3526. X. Eschalier, U. S. P. 995852. F. P. 374724, abst. J. S. C. I. 1907, **26**, 821. M. Fremery and E. Bronnert, U. S. P. 856857. See also D. R. P. 186766, 1904 (Ver. Glanzstoff Fabr.). M. Fremery, E. Bronnert and J. Urban, U. S. P. 804191, 1905; abst. J. S. C. I. 1905, **24**, 1251; see also D. R. P. 188113, 1905 (Ver. Glanzstoff Fabr., U. S. P. 806533, 1905, 806857, 1907). Levallois, Bull. Soc. Chim. 1885, **43**, 85. L. Lilienfeld, F. P. 399460, 1909; abst. J. S. C. I. 1909, **28**, 958; Chem. Ztg. Rept. 1909, 472. E. P. 8708, 1908; abst. J. S. C. I. 1909, **28**, 257. B. Loewe, Belg. P. 238479, 1911. O. Muller and Rheinische Kunstseide Fabrik, E. P. 18342, 1909; abst. J. S. C. I. 1910, **29**, 557. F. P. 405571, 1909; abst. J. S. C. I. 1910, **29**, 417. Muller, U. S. P. 836452. E. P. 10094, 1906. F. P. 365776. D. R. P. 187947. Aust. P. 33678. Swiss P. 42306. M. Prudhomme, F. P. 344138, 1904; abst. J. S. C. I. 1904, **23**, 1087. F. Beltzer Mon. Sci. 1908, (4), **68-69**, 657. J. Ubertin, F. P. 444462, 1911; abst. J. S. C. I. 1912, **31**, 1120; Kunst. 1913, **3**, 16. Soc. anonyme Soierres Nouvelles de Bruxelles, Belg. P. 186098, 1905. Soc. la Soie Artificielle du Nord, F. P. 437815, 1911. C. Wright, E. P. 737, 1883. A. Bardelli, Ital. P. 129734, 1913; abst. C. A. 1915, **9**, 2316. E. Bloch-Pimentel; U. S. P. 1044434, 1912, C. A. 1913, **7**, 221. E. P. 7893, 1912, C. A. 1913, **7**, 3227. British Cellulose Syn. Ltd. and V. E. Mertz, U. S. P. 954984. E. P. 1148, 1909; J. S. C. I. 1910, **29**, 24. F. P. 411592, 1910; J. S. C. I. 1910, **29**, 879. D. R. P. 250596, 1910; C. A. 1912, **6**, 3518; Zts. ang. Chem. 1912, **25**, 2382; Wag. Jahr. 1912, II, 441; Kunst. 1912, **2**, 359, 373. British Thomson-Houston Co., E. P. 8207, 1900; Kunst. 1913, **3**, 410. British Glanzstoff Manufacturing Co., Ltd., Kunst. 1912, **2**, 218.

partially soluble in the acid. With still stronger acid the effect is more marked, especially when the solution contains some zinc chloride, in which case considerable dissolving effect upon the cellulose takes place.

Our knowledge concerning the solubility in fuming hydrochloric acid dates back to 1856, in which year A. Bechamp[1] published his observations upon the solubility of cotton in concentrated acids such as hydrochloric acid, after the cotton was first converted into a pulp-like mass. In his later investigations upon optical activity A. Bechamp[2] made use of precipitation obtained by forming a solution of cellulose in cuprammonium with acetic acid. In general, however, the knowledge that concentrated hydrochloric acid has a dissolving action upon cellulose has remained useless for practical purposes because the fuming acid of commerce (37% to 38% absolute HCl) at ordinary temperature reacts only slowly and with great difficulty.

According to the patented method of R. Willstaetter,[3] hydrochloric acid of unusually high concentrations (which, however, cannot be obtained commercially but must be made by the evaporation of the technical varieties by the addition of hydrochloric acid gas at low temperatures), show an entirely different behavior with cellulose and cellulosic bodies. He appears to have succeeded with highly concentrated hydrochloric acids in obtaining solutions of cellulose, hydrocellulose, hydrated cellulose and oxycellulose, either from wood or from cotton cellulose, and suitable acids such as 40.8% to 41.4% HCl, yielding solutions containing from 12% to 15% of cellulose. According to this chemist's investigations, the limits of practicability are well beyond the strength of the ordinary acids of commerce, acids of

[1] Compt. rend. 1856, **42**, 1210; abst. Instit. 1856, 235; Ann. 1856, **100**, 367; Jahr. Chem. 1856, 674; J. prakt. Chem. 1856, **69**, 449; Kunst. 1913, **3**, 399.

[2] Compt. rend. 1884, **99**, 1027, 1122; 1885, **100**, 279, 368; abst. J. C. S. 1885, **28**, 237, 369; Bull. Soc. Chim. 1885, **43**, 661; Mon. Sci. 1885, **27**, 88, 218, 311, 317; Ber. 1885, **18**, R, 113, 141; Jahr. Chem. 1884, 303; Kunst. 1913, **3**, 399.

[3] U. S. P. 1141510, 1915; abst. C. A. 1915, **9**, 2311; Kunst. 1915, **5**, 240. E. P. 10605, 1914; abst. C. A. 1915, **9**, 2980; J. S. C. I. 1914, **33**, 859. F. P. 471479, 1914; abst. J. S. C. I. 1915, **34**, 349. D. R. P. Anm. W, 42345, 1913; abst. Kunst. 1913, **3**, 399, 400. D. R. P. 273800; abst. C. A. 1914, **8**, 2948; Chem. Zentr. 1914, I, 1904; J. S. C. I. 1914, **33**, 746. Holl. P. 1848, 1917; abst. C. A. 1917, **11**, 1300. R. Willstaetter and L. Zechmeister, Ber. 1913, **46**, 2401; abst. C. A. 1913, **7**, 3412.

sp. gr. 1.199 equivalent to 38.9% HCl being required, while an acid containing 39.5% HCl is exceptionally well suited for this purpose.

Hydrochloric acid at low and at room temperatures ordinarily acts only slowly upon cellulose, primarily by hydrolyzing it. For this reason the polyose may be precipitated into a gelatinous elastic mass by removing the excess of HCl gas or by diluting the solution with either water, alcohol, salt solutions or dilute acids or alkalis, and in this condition are suitable for the production of pure cellulose, cellulose esters and elastic substances, such as films, sheets, or artificial filaments.[1]

[1] The following examples are typical of carrying this method into effect: (1) 1 part of cotton is kneaded with 12 to 15 parts of hydrochloric acid (sp. gr. 1.209 at 15°) until a homogeneous viscous liquid, without residue is obtained. The HCl gas in excess is removed by suction and recovered together with some air bubbles. The solution is thereupon pressed through small orifices, water being used as the coagulating medium. (2) 1 part of cellulose is kneaded with 8 parts of hydrochloric acid (sp. gr. 1.212 at 15°) in a kneading apparatus until an almost clear viscous mass is formed, and the mixture allowed to stand for some time to reduce the viscosity. The coagulation of the cellulose is then brought about in any of the well known ways. (3) 1 part of wood meal is stirred for one-half hour with 7 parts of hydrochloric acid (sp. gr. 1.212 at 15°) at ordinary temperature, and then allowed to stand for one-quarter to one-half hour. The solution is then filtered off from the insoluble lignin, and precipitated or coagulated. This process is of peculiar interest in that it is stated that substantially the entire nitrocellulose supply of Germany during the recent war was obtained from wood pulp in a similar manner by dissolving it in Willstaetter's acid and reprecipitating the pure cellulose, which is then nitrated.

According to R. Willstaetter and L. Zechmeister (Ber. 1913, **46**, 2401; abst. C. A. 1913, **7**, 3412; Chem. Zentr. 1913, II, 1209; J. S. C. I. 1913, **32**, 822) whereas cellulose does not dissolve in ordinary concentrated hydrochloric acid of 1.19 density, but passes into solution with acid of density 1.204, 1.209 and 1.212 at 15°, corresponding to 39.9%, 40.8% and 41.4% HCl respectively, cotton or filter paper shaken with acid of 1.209 density dissolves clear in a few seconds at the room temperature.

By kneading the cellulose with a 1.212 gravity acid, a 15% solution can be obtained at room temperatures. These solutions are at first clear and colorless but after standing for a day a slight flocculent precipitate is formed which, upon further standing, becomes darker in color and finally a dark brown substance separates. Grape sugar behaves in the same way. By removing the HCl *in vacuo* the hydrolysis is retarded. The filtrate does not reduce Fehling's solution and acquires no reducing power on warming. Pine wood quickly dissolves and leaves 30% of its weight in lignin substances. 48% HBr gelatinizes cellulose, 57% acid dissolves it incompletely, whereas with 66% acid the cellulose goes completely into solution, even at zero degree. Concentrated hydriodic acid does not dissolve cellulose, whereas 70 to 75% HF gelatinizes and quickly dissolves it. From all these solutions, however, the cellulose can be re-precipitated, but in a changed condition.

In order to determine the amount of sugar formed, polarimetric measurements were made first on solutions with glucose and concentrated hydrochloric acid, and it was determined that before the hydrolysis is completed

Similar in many respects to the above described process, is the method of Z. Ostenberg,[1] in which concentrated sulfuric acid is added to cold (—10° to —15° C.) concentrated hydrochloric acid until the mixed acid is of such concentration that it will dissolve cellulose. For example, to 35% hydrochloric acid about 8 or 10% sulfuric acid is added so that the total strength if measured as hydrochloric acid in dissolving power would be about 41% to 42%. This acid will dissolve cellulose readily and differs from the Willstaetter solvent described above in that the latter employs hydrochloric acid only. The solution thus obtained is filtered through fine mesh copper screen and "spun" by squirting through microscopic perforations in a sheet of platinum or acid-resisting alloy into water. The resulting filaments are washed free from acid, bleached lightly and dried, the dried product being easy of nitration, resulting in the formation of a nitrocellulose of satisfactory stability and ballistic powers.[2]

Cellulose and Sulfuric Acid. It was in 1819 that H. Brac-

---

the polarimetric method gives higher values than the Fehling's Solution method (G. Bertrand, Bull. soc. chim. 1906, (3), **35**, 1285); abst. Chem. Zentr. 1907, I, 763; J. S. C. I. 1907, **26**, 60; Jahr. Chem. 1905–1908, II, 910, showing that the solution contains compound sugars. W. de Coninck and A. Raynaud (Bull. Acad. Roy. Belg. 1910, 587; abst. J. C. S. 1910, **98**, i, 654; C. A. 1911, **5**, 1585; J. S. C. I. 1910, **29**, 1299; Chem. Zentr. 1910, II, 1459; Jahr. Chem. 1910, II, 417) found that on macerating filter paper with concentrated hydrochloric acid at 28°, no reducing substance is produced, even after forty hours. If the paper is macerated during sixty-two hours and the mixture then heated at 95–96° during twenty minutes, it becomes brown but the filtrate does not reduce Fehling's solution. The brownish residue is partly soluble in ammonia and consists of humic matter. Cotton macerated during forty hours in hydrochloric acid shows no reduction, but after eighty-seven hours at 28.5, and then ten minutes at 95°–96°, shows copious reduction. It dissolves in fuming hydrobromic acid at 29° in a few minutes and the solution blackens on keeping. Such a solution gives a slight brownish black precipitate partly soluble in ammonia on dilution, and reduces Fehling's solution. See A. Leinveber, Kunst. 1918, **8**, 235; C. A. 1919, **13**, 1927. E. Rasser, Kunst. 1918, **8**, 97, 112; C. A. 1919, **13**, 1926.

[1] U. S. P. 1218954, 1917; abst. J. S. C. I. 1917, **36**, 450. U. S. P. 1242030, 1917; abst. J. S. C. I. 1917, **36**, 1174; C. A. 1918, **12**, 223. E. P. 104173, 1917; abst. J. S. C. I. 1918, A, **37**, 146; C. A. 1917, **11**, 1903. F. P. 484442, 1917; abst. C. A. 1918, **12**, 1123. In a later patent (U. S. P. 1315393, 1919; abst. C. A. 1919, **13**, 3035) Z. Ostenberg describes the production of glucose by dissolving cellulose in a mixture of HCl (35%) 9 parts, H_2SO_4, 0.5, and H_3PO_4 (85%) 2 parts. According to T. Fritsch (E. P. 6590, 1906; abst. J. S. C. I. 1906, **25**, 1006) paper is made resistant to water by passing the dry sized paper through a mixture of sulfuric and hydrochloric acids or sulfuric and nitric acids, or through hydrochloric acid or nitric acid alone. The excess of acid is then removed, and the paper is thoroughly washed. Writing on papers so treated cannot be removed easily by mechanical means, and the paper is also stated to be more durable.

[2] According to a modification of the Z. Ostenberg process (U. S. P.

onnot[1] observed that linen dissolved in concentrated sulfuric acid, and that if the linen was diluted with water, a clear solution resulted containing, besides sulfuric acid, another acid which he named *acide vegeto-sulphurique.* When the diluted solution was boiled for some hours a substance was produced which was fermentable, and which he consequently considered to be glucose.

In 1844 Blondeau de Carolles[2] investigated this acid, and found that when cotton was added to the concentrated acid, it dissolved and formed a light yellow solution which changed to dark violet upon standing. When the solution was diluted with cold water and neutralized with barium carbonate, the excess of acid was precipitated as the sulfate, while the barium salt of cellulose-sulfuric acid remained in solution; this was precipitated from the concentrated clear solution on adding strong ethyl alcohol. It was found that the composition of these salts varied with

---

1218953, 1917; abst. J. S. C. I. 1917, **36**, 450; C. A. 1917, **11**, 1545; Kunst. 1917, **7**, 261) cellulose is dissolved in a mixture of highly concentrated hydrochloric acid and a concentrated inorganic acid such as phosphoric acid, which does not react with the hydrochloric acid, at a temperature below 50°, not less than 25% of hydrogen chloride being present in the mixture.

The method of the Zellstoffabrik Waldhof and V. Hottenroth (Swiss P. 76329, 1917; abst. C. A. 1918, **12**, 1123. Dan. P. 23957, 1918; abst. C. A. 1919, **13**, 1390. D. R. P. 306818, 1917; abst. J. S. C. I. 1919, **38**, 131-A; Chem. Zentr. 1918, II, 327. Swiss P. 76329, 1917; abst. C. A. 1918, **12**, 1123. E. P. 132815, 1919) is somewhat similar to that above, in that a mixture of hydrochloric and sulfuric acids is claimed as especially energetic and efficacious as a solvent combination for cellulose, the total amount of HCl being less than 39%. Ten parts of ordinary concentrated HCl of density 1.19 (37.2% HCl) are mixed with one part of sulfuric acid (80% strength), and into this mixture—which contains 32.5% HCl to 10.1% H_2SO_4 is thoroughly incorporated one part of cotton, the mixture being cooled meanwhile. The cellulose in a short time dissolves to a clear viscous liquid, from which it may be obtained in filament form by expressing from nozzles into water as the precipitating medium. Or, into 8 parts of an acid mixture of 20% HCl and 18% H_2SO_4 is incorporated one part of cellulose by stirring, with cooling, a clear viscous solution being obtained after 15–20 minutes which may be precipitated either before or after filtration. According to W. de Coninck (Bull. Acad. Roy. Belg. 1910, 587; abst. J. S. C. I. 1910, **29**, 1299; Chem. Zentr. 1910, II, 1459; C. A. 1911, **5**, 1585; Jahr. Chem. 1910, II, 417) filter paper which has been subjected to the action of concentrated hydrochloric acid for 62 hours does not yield a product capable of reducing Fehling's solution. A product possessing cupric-reducing power is, however, formed by the action on cotton of concentrated hydrochloric acid for 87 hours, or of fuming hydrobromic acid for 24 hours.

[1] Ann. Chim. Phys. 1819, (2), **12**, 185; abst. Edin. Phil. J. 1820, **2**, 363; Gilb. Ann. 1819, **63**, 347; J. de Pharm. 1820, **6**, 416; Quart. J. Sci. 1820, **8**, 386; Schw. J. 1819, **27**, 328. A. Tilloch, Phil. Mag. 1820, **55**, 53, 118.

[2] Ann. 1844, **52**, 412; J. prakt. Chem. 1844, **32**, 427; **33**, 439; Rev. Sci. et Ind. **16**, 468; 1843, 69, 476; Berz. Jahr. 1846, **25**, 547, 582; Annuaire de Chemie, 1845, **1**, 468. See M. Honig and J. Schubert, Ber. 1885, **18**, 614.

the period the sulfuric acid solution of cellulose was allowed to stand before diluting.

About the same time[1] H. Fehling found the composition of one of the barium salts to be of percentage corresponding to $C_{90}H_{180}O_{90}BaO(SO_3)_2$. R. Marchand[2] acted on Swedish filter paper with sulfuric acid for four weeks, and obtained a lime salt, $C_{33}H_{28}O_8(SO_3)_2CaO$.

A. Bechamp[3] states that the substance obtained by dissolving cellulose in sulfuric acid is a dextrin-like starch dextrin—but with a lower specific rotatory power, and that on boiling this with acids a sugar is formed.

It is therefore apparent that for many years it has been recognized that concentrated sulfuric acid of certain strengths is capable of exerting a swelling or solvent action upon cellulose and its closely allied products. In 1891 R. Langhans[4] published his process for the manufacture of artificial filaments of cellulose dissolved in sulfuric and phosphoric acids, for which purpose cellulose is first subjected to a "purifying process" by treatment with an alkali and then with aqueous hydrochloric or sulfuric acids, afterwards washing with water until neutral and finally drying at about 40°. The cellulose is next impregnated with a solution consisting of aqueous phosphoric acid containing equivalent to 33% of phosphorus pentoxide and sufficient sulfuric acid so that the combined cellulose contains 20% H_2SO_4, using only enough to thoroughly saturate and impregnate the cellulose, the acid mixture being allowed to act until the fiber begins to swell and

---

[1] Ann. 1845, **53**, 135; **55**, 13; abst. Annuaire de Chemie, 1846, **2**, 486; J. prakt. Chem. 1845, **36**, 62; J. de Pharm. 1845, **8**, 477.

[2] J. prakt. Chem. 1845, **35**, 228. Terreil, J. C. S. 1873, **26**, 370.

[3] Compt. rend. 1856, **42**, 1210; abst. Instit. 1856, 235; Ann. 1856, **100**, 367; Jahr. Chem. 1856, 674; J. prakt. Chem. 1856, **69**, 449; Knsut. 1913, **3**, 399. E. P. 8260, 1911.

[4] U. S. P. 571530, 1896. D. R. P. 72572, 1891; 82857, 1893; abst. Jahr. Chem. 1895, 1362; Wag. Jahr. 1895, **41**, 957. F. P. 217557, 1891. Text. Col. 1897, **19**, 317; Ind. Text. 1897, **13**, 239. A. Herzheim, U. S. P. 591968, 1897. D. R. P. 86938, 1895. F. P. 252501, 1895. Belg. P. 118877, 1895, treats hydrocellulose with sulfuric acid or with cuprammonium, and afterwards with pyroxylin solution in the manufacture of water and grease proof paper. See also K. Hofman, D. R. P. 227198; Wag. Jahr. 1910, II, 431; Chem. Zentr. 1910, II, 1349; Kunst. 1911, **1**, 16. See W. Harrison, Jour. Soc. Dyers Col. 1912, **28**, 238; abst. Zts. Chem. Ind. Koll. 1913, **12**, 60; J. S. C. I. 1912, **31**, 679; C. A. 1913, **7**, 4077. S. Tschumanow, Zts. Chem. Ind. Koll. 1914, **14**, 321; abst. J. C. S. 1914, **106**, i, 932; C. A. 1914, **8**, 2971; J. S. C. I. 1914, **33**, 744; Chem. Zentr. 1914, II, 617.

pass into solution. The mass is then kneaded with sulfuric acid, and phosphoric acid added, when the dough is said to be transformed into a glass-like, transparent, viscid syrup, suitable for filament formation. It appears, however, that but little commercial use has been made of this process.

E. Berl[1] has found that cellulose or its closely allied derivatives may be used for the manufacture of artificial threads, filaments and plastic masses by treatment with sulfuric acid, if the temperature be kept continually very low (not exceeding —10° C.) the sulfuric acid being 60–77% H_2SO_4. Under these conditions, according to the patentee, the decomposing and dehydrating action of the sulfuric acid on the cellulose is restricted so as to be practically negligible and harmless. This advantageous influence of low temperature must be maintained during the entire process of coagulation, otherwise the decomposing action of the sulfuric acid predominates, resulting in the prepared products lacking in stability. It has been proven that the coagulation temperature must be nearly the same as or lower than the temperature for producing the solution to obtain products of commercial utility.[2]

[1] E. P. 4966, 1913; abst. J. S. C. I. 1913, **32**, 1063. D. R. P. 259248, 1912; abst. J. S. C. I. 1913, **32**, 653. Belg. P. 253945, 1913. D. Nagy Belg. P. 191460, 1906. S. Gwynn, U. S. P. 73322, 1868. J. Hanna, U. S. P. 198382, 1877. S. Haskin, U. S. P. 488967, 1892. E. Andrews, U. S. P. 312945, 1885. F. Taylor, U. S. P. 316847, 1885.

[2] As coagulants are recommended aliphatic alcohols, such as methyl and ethyl alcohol and their aqueous solutions, solutions of sulfates (such as ammonium sulfate), of phosphates, dilute sulfuric acid, the melting points of which are not above —10°. The following examples are illustrative of carrying the process into effect:

(*a*) One part of cool, dry, and finely divided cotton is digested in the kneading machine with 12 parts of 74% sulfuric acid and not above —15°, and then left standing for some time, when a viscous mass is obtained; the confined air can be exhausted *in vacuo* and after filtration of this mass coagulation is caused by immersion in 50% alcohol and cooled to —20°.

(*b*). One part mercerized cotton is thoroughly mixed with 12 parts 70% sulfuric acid in a kneading machine at not exceeding —15° until it has swollen to a viscous mass, coagulation being obtained by a 60% solution of methyl alcohol reduced to a low temperature.

(*c*) Hydrocellulose is digested with sulfuric acid as described above until a homogeneous viscous mass is obtained, coagulation being brought about by 25% sulfuric acid cooled almost to its freezing point.

(*d*) Finely divided, carefully dried wood cellulose is digested with cooled 65% sulfuric acid until a homogeneous mass is obtained, this being coagulated by a solution of 38.5% by weight of ammonium sulfate cooled to —18°.

E. Cunningham and F. Thiele (U. S. P. 637090, 1899; abst. Mon. Sci. 1900, **56**, 139) have described the preparation of a synthetic gum, having the adhesive characteristics of gum arabic, and produced by treating cellu-

A. Stern has made a comprehensive study of the action of sulfuric acid on cellulose and correlated the work of previous investigators in this field.[1]

The process of X. Karcheski, which consists in the treatment of cloth or other textile vegetable fibers, either alone or united with paper or a similar fibrous material by means of sulfuric acid, in which the textile is first immersed in a bath of sulfuric acid until the fiber has been partially dissolved,[2] and a similar process of L. Grote[3] have apparently not been developed commercially.

lose (lint) with sulfuric acid of not less than 1.842 sp. gr. at a temperature not exceeding 40° F., the "cellulose tetrasulfate" thus formed uniting with water in the presence of potassium pyrosulfate which is also used, the sulfuryl groups in the cellulose tetrasulfate being eliminated and arabic acid formed.

1. Proc. Chem. Soc. 1894, 186; J. C. S. 1895, **67,** 74; abst. J. S. C. I. 1894, **13,** 1230; Bull. Soc. Chim. 1896, (3), **16,** 1081; Ber. 1895, **28,** R, 462; Jahr. Chem. 1895, **48,** 1358; Meyer Jahr. Chem. 1895, **5,** 145, 524; Chem. News, 1894, **70,** 267; Chem. Centr. 1895, **66,** I, 29; Jahr. Chem. 1894, **47,** 1132. Proc. Chem. Soc. 1904, **20,** 43; J. C. S. 1904, **85,** 336; abst. Chem. News, 1904, **89,** 117; J. S. C. I. 1904, **23,** 265; Bull. Soc. Chim. 1904, **32,** 1175; Chem. Centr. 1904, **75,** I, 934, 1405; Chem. Ztg. 1904, **28,** 246; Jahr. Chem. 1904, **57,** 1161. In this connection see Proc. Chem. Soc. 1904, **20,** 90; J. C. S. 1904, **85,** 691; abst. Chem. News, 1904, **89,** 235; J. S. C. I. 1904, **23,** 557; Bull. Soc. Chim. 1904, **32,** 1301; Rep. Chim. 1904, **4,** 293; Chem. Centr. 1904, **75,** I, 1557; Jahr. Chem. 1904, **57,** 1161. See also M. Hoenig and S. Schubert, Monatsh. 1885, **6,** 708; 1886, **7,** 455; abst. Wein. Akad. Ber. **92,** (2 Abth.), 737; Bull. Soc. Chim. 1886, (2), **46,** 517; Ber. 1885, **18,** 614; Jahr. Chem. 1885, **38,** 1376. Allihn, J. prakt. Chem. 1880, **130,** 61. J. v. Kalinowsky, J. prakt. Chem. 1845, **35,** 193; J. de Pharm. 1845, **8,** 309.

2. X. Karcheski, U. S. P. 137451, 1873. Refer to Chemische Fabrik auf Aktien, D. R. P. 86938, 1895; Ber. 1896, **29,** R, 610.

3. E. P. 23728, 1912; abst. J. S. C. I. 1913, **32,** 1104; C. A. 1914, **8,** 1346. E. Bert, Ital. P. 134462, 1913; C. A. 1915, **9,** 2710.

The parchmentizing effect of sulfuric acid is probably explained from the fact that the cellulose becomes dissolved superficially due to the action of the sulfuric acid, this action penetrating to a certain depth in the paper. Upon washing the treated surface the dissolved cellulose becomes precipitated in the interstices of the paper, as it were, and cements the individual cellulose fibers more firmly together into an apparently homogeneous mass. This cementation of the paper undoubtedly explains its increase in strength, and translucent appearance. When paper thus treated is moistened it loses its toughness and rigidity and can be considerably expanded without rupture. If stretched tight and allowed to dry, it regains its corneous structure again. By reason of this property it finds considerable use for capping the stoppers of bottles.

For additional data on the development of parchment and pergament paper, see: Smith, Lond. J. Conj. S. U. **45,** 177. Weinmann, Dingl. Poly. 1855, **136,** 159. Bayer, Kunst. u. Gewerbebl. 1855, 365. Gaine, Dingl. Poly. 1857, **144,** 154; Monit. Ind. 1857, No. 2152, 2336; Mech. M. V. **66,** 445; Chem. Centr. 1857, 892; Pr. Mech. J. (2), **3,** 175. Hofmann, Chem. Centr. 1859, 614; Dingl. Poly. 1859, **152,** 380. Bayer, Kunst. u. Gewerbebl. 1859, 297. Jennings, Rep. of Pat. **34,** 391; Ann. **112,** 243; Hannover Mitth. 1860, 51; Bull. soc. Encourag. 1860, 690; Chem. Centr. 1860, 56; Dingl. Poly. 1860, **155,** 388; J. prakt. Chem. 1859, **78,** 488. Taylor, Lond. J. N. S

Unless the action of sulfuric acid upon cellulose be carefully regulated as to concentration and temperature, sulfuric acid produces amyloid (mentioned elsewhere), and this fact is utilized in the manufacture of what is known as "vegetable parchment," which product is obtained by a short immersion of unsized paper in 75–85% sulfuric acid, followed by immediate thorough washing and drying. The effect of this treatment is to cause the formation of gelatinous amyloid on the surface of the paper,[1]

10, 351; J. prakt. Chem. 1859, **78**, 207; Dingl. Poly. 1860, **155**, 397; Wieck's Gwz. 1860, 250; Bayr. Kunst. u. Gewerbe. 1860, 125. Reinsch, Dingl. Poly. 1860, **156**, 156; Wieck's Gwz. 1860, 249; Chem. Centr. 1860, 1199; Bull. Soc. Encourag. 1860, 692; Bayer. Gewerbeztg. 1860, No. 8; Pharm. Centralh. 1860, No. 48; Chem. Tech. Mitth. 1859–1860, 115. V. Kletzinsky, Pharm. Centralh. 1860, **2**, No. 3; Stamm's illust. Wochensch. 1860, No. 16; Chem. Tech. Mitth. 1859–1860, 113; Dingl. Poly. 1860, **156**, 385; Chem. Centr. 1860, 911; Wieck's Gwz. 1860, 319. Dullo (product called Papyrine), Dingl. 1860, **158**, 392; Chem. Centr. 1861, No. 2; Poly. Notiz. 1861, No. 3; Chem. Tech. Mitth. 1860–1861, 120. Hoffmann, Ann. 1859, **112**, 243; Pharm. Centralh. 1860, 377; Dingl. Poly. 1860, **155**, 388; Bayer. Kunst. u. Gewerbebl. 1860, 125; Poly. Centr. 1860, 120; Chem. Tech. Mitth. 1859–1860, 116. Ferwer, Dingl. Poly. 1861, **159**, 218; Chem. Centr. 1861, 543; Bayer. Kunst. u. Gewerbebl. 1861, 425. Brandegger, Dingl. Poly. 1862, **163**, 467; Bayer. Kunst. u. Gewerbebl. 1862, 101; Chem. Centr. 1862, 830. Graham, Wieck's Gwz. 1862, 87; Chem. Centr. 1862, 551; Phil. Mag. (4), **23**, 290; Deutsch. Ind. Ztg. 1862, 321. Vogel, Wieck's Gwz. 1862, 258; Chem. Centr. 1862, 1244. Sauerwein, Chem. Centr. 1862, 1101; Wieck's Gwz. 1862, 313. Winter, Chem. Centr. 1863, 1595. Gaedicke, Zts. d. V. deutsch. Ingen. 1864, 345. Jacobsen, Pharm. Centralh. 1865, No. 3; Chem. Tech. Repert. 1864, II, 29; Industriebl. 1865, No. 1, 2, 3; Poly. Notiz. 1865, No. 5; Poly. Centr. 1865, 461; Dingl. Poly. 1865, **176**, 167; Chem. Tech. Mitth. 1864–1865, 159.

[1] For general discussion on the effect of sulfuric acid in dissolving cellulose, see W. Zaenker, Kunst. 1916, **6**, 17; abst. C. A. 1916, **10**, 971; Zts. ang. Chem. 1916, **29**, R, 182; J. S. C. I. 1916, **35**, 596. Cf. C. A. 1907, **1**, 1696, 2174; 1914, **8**, 1675, 2219.

The behavior of sulfuric, phosphoric and hydrochloric acids of varying concentration towards cellulose in the form if surgeon's cotton purified by treatment with 1% sodium hydroxide, has been studied by A. Leighton (J. Phys. Chem. 1916, **20**, 182; abst. J. C. S. 1916, **110**, ii, 128, 226; J. S. C. I. 1916, **35**, 464; C. A. 1916, **10**, 1296). He treated one gram of cellulose with 100 cc. acid for three hours, then centrifugalized for an hour, gravimetrically, estimating the acid retained by the cotton. Curves were plotted illustrating the increase in absorption with increasing concentration of acid and it was found that selective absorption is shown only at high concentration and is most marked in the case of hydrochloric acid; with sulfuric acid it begins at a concentration of 400 grams per liter, and it is not detected with phosphoric acid. The value of the absorption expressed in grams is greatest with sulfuric and least with hydrochloric acid. No evidence of the formation of a compound between acid and cellulose was discovered. The presence of acid lowers appreciably the amount of water absorbed by the cotton.

For methods of testing imitation parchment papers, consult G. Schacht, Wochbl. Papierfabr. 1911, **42**, 3632; abst. C. A. 1912, **6**, 684; J. S. C. I. 1911, **30**, 1206. For the action of concentrated sulfuric acid on cellulose, see L. Sabattani, Koll. Zts. 1914, **14**, 29; abst. Chem. Zentr. 1914, I, 2033; C. A. 1914, **8**, 1690.

which, in appearance, resembles natural parchment. Artificial horse hair has been prepared from certain Mexican grasses in a somewhat similar manner.

As stated under the topic "Mercerization," concentrated mineral acids under proper conditions of treatment have a mercerizing action upon cellulose fibers, which by the hydrating treatment possess an increased affinity for dyestuffs, acquires an increased luster and additional strength. If the action of the acid be prolonged, complete destruction of the fiber occurs.

Action of Zinc Chloride on Cellulose. Concentrated solutions of neutral zinc chloride are capable of dissolving cellulose only after prolonged digestion at 80° to 100°, although by first treating the cotton with alkalis, solution occurs much more readily and in the cold. This solution of cellulose is not a simple phenomenon, but is attended both with hydrolysis and condensation, the former being shown by reduction of Fehling's solution and the latter evidenced by the formation of furfural and similar bodies obtainable by diluting the original solution and filtering from the re-precipitated cellulose.

Cross and Bevan have observed that when experiments upon cotton cellulose have been carefully conducted, solution and re-precipitation may occur with a loss of not over 1% in weight of cellulose. This phenomenon of the solution of cellulose in zinc chloride has many industrial applications. As far back as 1884 J. Wynne and L. Powell[1] dissolved cellulose in a solution of zinc chloride, bromide or iodide, or bismuth chloride or bromide, or mixtures of these, and then freed the solution from air by heating in a chamber connected with an exhaust pump. The cellulose was then precipitated by squirting the solution through a small orifice and the threads used for the production of carbon filaments for incandescent electric lamps, insulating materials and woven fabrics. Previous to this, Persoz[2] had discovered a substitute

---

[1] E. P. 16805, 1884; abst. J. S. C. I. 1886, **5**, 172. Lane-Fox was the first to patent electric light carbons made by carbonizing parchmentized cellulose (zinc chloride treatment). He used a vulcanized fiber as also did Swan, quite independently. Compare also T. Taylor, E. P. 787, 1859; abst. Lond. Jour. Arts, 1859, 351; Poly. Centr. 1860, 207; Pharm. Centrahalle, 1860, No. 45; Dingl. Poly. 1860, **155**, 397; Polyt. Notiz. 1860, 98; Chem. Tech. Mitth. 1859–1860, 115. G. Robertson, E. P. 4630, 1877.

[2] Poly. Centr. 1867, 617; abst. Chem. Centr. 1867, 448; Chem. Tech. Rep. 1867, I, 95; D. Indztg. 1867, 5. W. Courtenay, U. S. P. 193322, 193323, 1877. H. Tiffany, U. S. P. 1226279; C. A. 1917, **11**, 2155.

for collodion valuable to photographers, by dissolving a solution of silk in a mixture of zinc chloride neutralized with zinc oxide.

E. Manby[1] sized fabrics by treating cellulose dissolved in zinc chloride, the finishing material being especially applicable, according to the patentee, in calico printing and dyeing mixed with coloring liquids or with mordants or applied to the fabric or yarn preparatory to the dyeing process.

The so-called fiberless thread of J. Hoyne[2] consists in dissolving cellulose in a designated solution of a zinc salt, filtering the cellulose and passing the solution under pressure through a thread-forming medium into a coagulating compound, which, after washing, was dried in the usual manner.

W. Dreaper,[3] W. Dreaper and H. Tompkins[4] and H. Tompkins and W. Crombie[5] have converted cellulose into hydrocellulose either by treatment with a strong solution of sodium hydroxide without any bleaching process, or by steeping it in a solution of zinc chloride of 10° Tw. and then heating. The hydrocellulose thus obtained is then dissolved in a solution of zinc chloride, preferably made distinctly acid to facilitate solution, which solution is then forced through fine openings into a coagulating bath of either strongly alkaline solution to which ammonium chloride or ammonia is added to prevent precipitation of the zinc compounds, or a concentrated solution of a suitable salt as sodium sulfate, either with or without the addition of alcohol.

In the W. Werner inventions,[6] the process of A. de Madaillon,[7] C. Mueller and D. Wolf,[8] and Y. Ogawa and S. Okubo,[9] cotton

---

1. E. P. 943, 1894; abst. J. S. C. I. 1895, **14**, 568. See also E. P. 10466, 1894; abst. J. S. C. I. 1895, **14**, 569. F. P. 308715, 1901.
2. U. S. P. 625033, 1899. E. P. 17901, 1897. D. R. P. 113, 786; abst. Chem. Centr. 1900, II, 1043. A. Hill, E. P. 8076, 1901. F. P. 320614.
3. E. P. 858, 1908; abst. J. S. C. I. 1909, **28**, 201.
4. E. P. 10487, 17901, 1897; abst. J. S. C. I. 1898, **27**, 573, 841. Belg. P. 135251, 1898. E. P. 12259, 1911. J. Strehli, U. S. P. 717050, 1902.
5. E. P. 28712, 1904; abst. J. S. C. I. 1906, **25**, 119.
6. U. S. P. 697580; abst. J. S. C. I. 1902, **21**, 614. E. P. 1850, 1901; abst. J. S. C. I. 1902, **21**, 771.
7. F. P. 345012, 1904; abst. J. S. C. I. 1904, **23**, 1206. F. Ahrens, D. R. P. 216629, 1907; Mon. Sci. 1911, (5), **74**, 63; Zts. ang. Chem. 1910, **23**, 144; Chem. Zentr. 1910, **81**, I, 71; Chem. Tech. Rep. 1909, **33**, 664; Chem. Ind. 1909, **32**, 837; J. S. C. I. 1910, **29**, 36; C. A. 1910, **4**, 827.
8. U. S. P. 931634, 1909; abst. J. S. C. I. 1909, **28**, 1001; C. A. 1909, **3**, 2627. E. P. 6942, 1906; abst. J. S. C. I. 1906, **25**, 775. E. P. 10430, 1912; abst. J. S. C. I. 1913, **32**, 531. F. P. 443133, 1912; abst. J. S. C. I. 1912, **31**, 1026. F. Muller, Belg. P. 211349, 1908. Swiss P. 35911.
9. Jap. P. 31374, 1917; abst. C. A. 1918, **12**, 224. F. P. 489330, 1918.

cellulose is dissolved in saturated zinc chloride solution at a temperature of 80° to 100°, the cellulose being afterwards regenerated by precipitation in a suitable coagulating medium.

In the well-known process of E. Bronnert[1] the clean cellulose is treated successively with a concentrated solution of caustic alkali at a low temperature, together with an oxidizing and bleaching agent and subsequently dissolved in concentrated zinc chloride solution without the application of heat. A rather viscous solution is thus obtained containing approximately 8% of cellulose. The solution thus formed may either be used by itself or combined with a solution of natural silk waste dissolved in the usual manner in a solution of zinc chloride, the mixture being especially applicable for printing and coating fabrics and in the manufacture of threads. For the latter purpose, however, the amount of silk solution in the mixture should, according to the patentee, not exceed one-fifth that of the cellulose. The printed or coated fabric is passed through a bath containing dilute acid or a 10% solution of ammonium chloride and dried in a stretched

---

Can. P. 187349, 1918; abst. C. A. 1919, **13**, 186. E. P. 122527, 1919; abst. C. A. 1919, **13**, 1764; J. S. C. I. 1919, **38**, 170-A.

The essence of their invention lies in using saturated solutions of zinc chloride and elevated temperatures, in order to reduce the dissolving time. Whereas ordinarily, cellulose is warmed with $ZnCl_2$ solution of sp. gr. 1.8–1.88 at or below 80°, the temperature being raised when the cellulose becomes gelatinized, this method requires several hours to completely effect solution, and in consequence of this long period of heating the cellulose solution is prone to become dark colored. The patentees take 100 gm. $ZnCl_2$ of sp. gr. 1.915 at 30°, add solid zinc chloride in amounts so that when the solution is subsequently heated to 65°, the solution is still saturated. When the solution is raised to 100°, 5 gm. absorbent cotton is added, complete solution resulting in less than half an hour.

In Jap. P. 31625, 1917; abst. C. A. 1918, **12**, 534, Y. Ogawa, S. Okubo and N. Satake mix a solution of cellulose in zinc chloride with a solution of cane or grape sugar, or a mixture of starch and dextrin, the resulting mixture being extruded through a very small opening in a glass nozzle into alcohol as the precipitant, a satisfactory artificial silk, according to the patentees, being thereby produced. See F. P. 489330; La Papeterie, 1919, **12**, 80; Paper, 1919, **25**, 24.

[1] U. S. P. 646799; abst. Mon. Sci. 1900, **56**, 219. E. P. 18260, 1899; abst. J. S. C. I. 1900, **19**, 659. F. P. 292988; abst. Mon. Sci. 1900, **56**, 224; Chem. Ztg. 1900, **24**, 572; Rev. Chim. 1900, **2**, 111, 268, 351. D. R. P. 118836, 1899; abst. Chem. Zts. 1901–1902, **1**, 186; Chem. Centr. 1901, I, 714; 1901, II, 514; Chem. Ztg. 1901, **25**, 252. Belg. P. 145281, 1899. See also: Bull. Soc. Mulhouse, 1900, 177; abst. J. S. C. I. 1900, **19**, 819, 820; Jahr. Chem. 1900, 843; Chem. Centr. 1900, II, 740. Aust. P. 11066; abst. Chem. Centr. 1901, I, 714. See also, Bayerisches Ind. und Gewerbe. Blatt. 1891, **23**, 476; Gummi, Ztg. 1891, No. 13.

condition, and which does not admit of additional treatment.

Vulcanized Fiber.[1] In addition to the industrial applications of the zinc chloride solutions of cellulose for artificial filaments, fiber treated with a solution of zinc chloride is known as vulcanized fiber, the resulting gelatinous mass obtained being manufactured into various articles, such as blocks and sheets. The chief difficulty encountered where large articles are obtained in this manner, is the subsequent removal of the zinc salt, this latter necessitating a most thorough and lengthy process of washing. The material may be rendered more waterproof by a further process of nitration.

L. Collardon[2] manufactures a plastic material as a substitute

---

[1] F. Taylor, E. P. 10864, 1884; abst. J. S. C. I. 1885, **4,** 115; renders vulcanized fiber pliable by submitting it to a bath of a deliquescent salt combined with glycerol. H. Arledter (E. P. 2018, 1910; abst. J. S. C. I. 1911, **30,** 205; F. P. 418584, 1910; abst. J. S. C. I. 1911, **30,** 80; E. P. 16085, 1912; abst. J. S. C. I. 1913, **32,** 865) has described a process of treating cellulose in which the air is preferably ozonized, and in which aluminum sulfate or other parchmentizing compound is added to the mixture, the treatment being continued until a jelly-like mass has been formed. The T. Kelley cellulose composition for an india-rubber substitute is described in E. P. 19853, 1910; abst. J. S. C. I. 1912, **31,** 83; C. A. 1912, **6,** 1503. Celluvert (G. Springer, Gummi Ztg. 1901, **15,** 329; abst. J. S. C. I. 1901, **20,** 602) is a hydrocellulose impregnated with zinc chloride, first produced in the United States in 1878, and patented in England by H. Morrow (E. P. 9319, 1885; abst. J. S. C. I. 1885, **4,** 751; U. S. P. 322629; abst. Wag. Jahr. 1885, **31,** 1043). The "elamite," of G. Robertson, E. P. 4630, 1877, is similar. A zinc chloride treated paper was patented by T. Taylor as early as 1859 (E. P. 787, 1859), Lond. Jour. Arts, 1859, 351; Poly. Centr. 1860, 207; Pharm. Centralh. 1860, No. 45; Dingl. Poly. **155,** 397; Poly. Notiz. 1860, 98; Chem. Tech. Mitth. 1859–1860, 115.

[2] F. P. 372584, 1906; abst. J. S. C. I. 1907, **26,** 539. U. S. P. 953319, 1910; abst. C. A. 1910, **4,** 1530; J. S. C. I. 1910, **29,** 557. H. Stassen, Belg. P. 254057, 1913, agglomerates cellulose materials to replace leather by zinc chloride followed by cuprammonia. See E. Krusche, E. P. 8164, 1899; abst. J. S. C. I. 1899, **18,** 756, who prepares vulcanized fiber with cuprammonia. Vulcanized Fibre Co., E. P. 1008, 1877. See Papier Ztg. 1905, 3183; 1908, 3330. T. Hanna, U. S. P. 196894, 196895, 1877. In the F. Ahrens process for vulcanized fiber manufacture (Papierfabr. 1913, **11,** 1414; abst. J. S. C. I. 1913, **32,** 1152; C. A. 1914, **8,** 1203) boiled cotton or linen rags are beaten in presence of sodium carbonate to a long-fibered half-stuff. The pulp is drained and washed in centrifugal machines, in which also the short-beaten fiber-fragments are eliminated. The stuff is mixed with a dilute solution of zinc chloride and formed into boards of spongy texture. Single boards are laid flat in stoneware trays, covered with a concentrated solution of zinc chloride and allowed to remain protected from the air for some hours. The excess of liquid is drained off and the surface of the sheet is strewn with a layer of finely powdered, fused zinc chloride, several mm. thick. When the powder has dissolved, the action can be accelerated by slight and uniform heating in an electrically heated oven, in which the temperature at all points can be carefully controlled. At first the temperature must not exceed 40°, but after an hour it may be raised to 60°–70°. The board becomes

for felt, leather or cork by pressing and drying a mixture of comminuted organic fibers as cotton, cork or wood meal in a solution of cellulose in zinc chloride as the cementing material. In hardening cotton fiber sheets or other fibrous material, H. Tiffany[1] immerses in a bath of zinc chloride which softens or gelatinizes the cellulose of the fiber, which is then electrolyzed to remove the acid or salt retained by the fabric, the latter being then slowly dried in order to harden.[2]

In the A. Parkes process[3] zinc iodide or nitrate have been specified as preferable to the corresponding chloride, while in the method of C. Mueller[4] zinc chlorate is advocated, especially where the filaments are to be used in the production of incandescent mantles. If a gelatin or celluloid substitute is to be manufactured a hardening agent such as formaldehyde, may be added during the boiling process, the resulting mass being treated, if necessary, with calcium chlorate solution and afterwards rolled into filaments or sheets.

Along similar lines is the process of J. Strehli,[5] whereby materials similar to vulcanized fiber, gelatinized fiber, and leatheroid are obtained by treatment of cellulose first with zinc chloride (or the chlorides of tin, calcium, magnesium or aluminum) in order to render the cellulose more dense and less porous. The next step in the process consists in incorporating some body which tends to induce flexibility, such as sugar, glycerol and water, the

---

vitreous and smooth. The tray is removed, the board allowed to cool and absorb moisture from the air, and the lye poured off and replaced by water. The sheet gradually hardens and is allowed to drain on a glass plate. Washing is continued in a tank of water in which the sheet is suspended on lead-covered wire netting, and is completed in running water. The sheet is dried slowly at 60°-100°, if necessary with the help of a vacuum. It is finally pressed flat and constitutes a product which is pale yellow in color, fairly transparent at a thickness of 1 cm. and possesses all the properties of the best vulcanized fiber. The zinc chloride is recovered to the extent of 90% and the fine particles of fiber from the centrifugal machines are collected in filter-presses and used as a filling for vulcanite goods. Compare D. R. P. 216629, 1907; abst. C. A. 1910, **4**, 827; Chem. Zentr. 1910, I, 71; Zts. ang. Chem. 1910, **23**, 144.

[1] U. S. P. 1226279, 1917; abst. C. A. 1917, **11**, 2155; J. S. C. I. 1917, **36**, 708.

[2] Compare C. Cross and E. Bevan, Cosmos, 1893, **26**, 288.

[3] E. P. 983, 1881. D. R. P. 18413, 1882; abst. Dingl. Poly. 1882, **245**, 141; Wag. Jahr. 1882, **28**, 1061; Chem. Tech. Rep. 1882, **21**, I, 83; Chem. Tech. Mitth. 1882-1883, **32**, 84, 278; Chem. Ind. 1882, **5**, 48.

[4] E. P. 10430, 1912. F. P. 443133, 1912; abst. J. S. C. I. 1912, **31**, 1026; 1913, **32**, 531.

[5] U. S. P. 717050, 1902; abst. J. A. C. S. 1903, **25**, 344.

material being then heated with a fusible binding agent as resin, gum or shellac, for the formation of thermoplastic, moldable articles.

According to La Compagnie Francaise de la Soie Parisienne,[1] elastic cellulose fibers of great tensile strength and capable of replacing silk are obtained from solutions of cellulose in zinc chloride or ammoniacal cupric chloride, when the separation of the individual filaments is effected by moderately concentrated sulfuric acid of 30–65% strength. The best results are claimed to be obtained at the ordinary temperature with 50% acid. The threads produced with a more dilute acid are weaker and less pliant, while the employment of acid of higher concentration than 65% results in the partial disintegration of the product.

A. Hill[2] imparts to mercerized cotton yarns and tissues the plasticity necessary to enable them to receive and retain—like silk fabrics—forms impressed upon them in the operations of crimping, by treatment with a solution of cellulose in zinc chloride and calcium chloride, the fabrics or tissues being then passed through alcohol to precipitate the cellulose and remove the solvents. Or, they may be coated with casein, or gelatin followed by a formaldehyde bath to render the proteid insoluble, in some instances increasing the water-repellent effect by a final treatment with celluloid dissolved in acetone or other readily evaporable liquid.

Other Cellulose Solvents. According to A. Dubosc,[3] cellulose readily dissolves in the thiocyanates (sulfocyanides) forming a viscous material like collodion, which is adapted to form threads and may be used in the manufacture of artificial silk.

In a recent patent disclosure[4] is described a process for the treatment of cellulose in the production of solutions and viscous

---

[1] F. P. 308715, 1901; abst. J. S. C. I. 1902, **21**, 49. See also, C. Suevern, Faerb. Ztg. 1900, **11**, 97; abst. J. S. C. I. 1900, **19**, 436. E. Bronnert, Bull. Soc. Ind. Mulhouse, 1900, 177; abst. J. S. C. I. 1900, **19**, 819, 820; Jahr. Chem. 1900, 843; Chem. Centr. 1900, II, 749.

[2] E. P. 8076, 1901. U. S. P. 705244, 1902. F. P. 320614, 1902; abst. J. S. C. I. 1902, **21**, 912, 1074; 1903, **22**, 42.

[3] Bull. soc. ind. Rouen; Chem. Ztg. 1905, **29**, 823; abst. J. S. C. I. 1905, **24**, 901. Bull. soc. ind. Rouen, **33**, 318; abst. Muster. Ztg. **53**, 19. Bull. soc. ind. Rouen, 1908, **36**, 272; C. A. 1908, **2**, 3283.

[4] Manchester Oxide Co., R. Clayton, J. Huebner, and H. Williams, E. P. 123784, 1919; abst. J. S. C. I. 1919, **38**, 282-A; C. A. 1919, **13**, 1637. U. S. P. 1301652, 1919; abst. J. S. C. I. 1919, **38**, 460-A; C. A. 1919, **13**, 1928.

and gelatinous bodies, which is brought about by the treatment of cotton and other forms of cellulose with thiocyanates. The thiocyanates of manganese, strontium, calcium and lithium will of themselves act satisfactorily, while in other cases best results are obtained by employing two or more thiocyanates simultaneously, as by dissolving sparingly soluble thiocyanates in solutions of more soluble thiocyanates or in calcium chloride—the latter having no adverse effect on the solvent action of the thiocyanates for cellulose. The thiocyanate solutions may be acidified, preferably with acetic acid. The method of carrying the process into effect is indicated by the following examples:

1. Four gm. of cotton, preferably dry, is placed in 100 cc. of calcium thiocyanate solution of sp. gr. 1.38, the mixture is stirred, heated to 100° and the heating continued for one hour with agitation, the temperature being afterwards raised to 120°, and there maintained until solution of the cellulose results.
2. Proceed as in Example 1, the solvent mixture being 100 cc. containing 70 gm. each of sodium and mercuric thiocyanate.
3. Thirty cc. of calcium chloride solution containing 86 gm. $CaCl_2$ per 100 cc. of solution is added to 70 cc. calcium thiocyanate solution containing 76 gm. per 100 cc. of solution. The liquids after thorough mixing, are used as in Example 1 above.

Acetic acid of 4% strength may be added to the above.

In the process for the production of new derivatives as disclosed by P. Goissedet[1] cellulose, such as cotton, preferably in the dry condition, or cellulose derivatives containing hydroxyl groups, is made to react with an aliphatic or aromatic isocyanic ester, with or without the addition of a tertiary base or bases, to produce carbamic esters, which can be used for the same purpose as other cellulose esters. Thus, dried cellulose may be heated with about three times its weight of phenyl isocyanate or other isocyanic ester, in presence of anhydrous pyridine (which promotes the reaction and acts as a diluent), and the resulting phenylcarbamic ester is isolated by pouring the mass into water.

According to H. Deming[2] strong solutions of mercuric chlor-

---

[1] E. P. 130277, 1919; abst. J. S. C. I. 1919, **38**, 714-A.

[2] J. A. S. C. 1911, **33**, 1515; abst. J. S. C. I. 1911, **30**, 1111; J. C. S. 1911, **99**, i, 771; C. A. 1911, **5**, 3678; Chem. Zentr. 1911, II, 1433; Koll. Zts. 1911, **9**, 200; Zts. Chem. Ind. Koll. 1912, **11**, 43. P. v. Weimarn (D. R. P. 275882, 1912; abst. J. S. C. I. 1914, **33**, 958; C. A. 1915, **9**, 378; Zts. ang.

ide and bismuth chloride in concentrated hydrochloric acid form splendid solvents of cellulose, even in the cold. Four parts of stannous chloride dissolved in one part of water brings cellulose

Chem. 1914, **27**, 603; Chem. Ztg. Rep. 1914, **38**, 434; Wag. Jahr. 1914, II, 413) has embodied these ideas in a patent, the essence of which is the conversion of cellulosic substances first into a gelatinous or plastic condition and finally into colloidal solutions, by heating them under suitable conditions with solutions of neutral salts, other than zinc salts, potassium and ammonium thiocyanate, potassium iodide, and potassium-mercuric or barium-mercuric iodide. When sodium iodide, calcium bromide or iodide, or barium, calcium, strontium, or sodium thiocyanate is used, the reactions can be carried out at atmospheric pressure. Sodium or potassium chloride and sodium sulfate involve the use of higher pressures. When "concentrated" sodium chloride solution is used, solution of the cellulose commences at about 170° at 8 atmos. The same solvent action is observed with nitrates, acetates, and many other salts. P. von Weimarn (Zts. Chem. Ind. Kol. 1912, **11**, 41; abst. J. S. C. I. 1912, **31**, 768; C. A. 1912, **6**, 3516; J. C. S. 1912, **102**, i, 679; Chem. Zentr. 1912, II, 817; Chem. Ztg. Rep. 1913, **37**, 14) has found that different kinds of cellulose (filter-paper, pure cotton wool) can be converted into a gelatinous, plastic condition or into a dispersoid (colloidal) solution by simple treatment with aqueous salt solutions, if certain conditions of concentration, pressure, temperature, and duration of action, varying according to the nature of the salt, be maintained. The more soluble the salt and the greater its capacity of forming hydrates, the more readily soluble (peptizable) is the cellulose in the solution; hence it is generally advisable to increase the solubility by increasing the pressure or temperature, or both. In carrying out this peptization process, a vessel is filled with water, the cellulose, *e. g.*, filter-paper (3 gms. per 100 cc. of water) is introduced, and a suitable salt (lithium chloride, calcium bromide, manganese thiocyanate, etc.) is added, while the contents of the vessel are heated. After a time the conversion of the cellulose into a gelatinous, plastic condition begins and may be accelerated by agitating the mixture. When the desired condition has been attained, the heating and addition of the salt are stopped, the mixture is cooled, the solution decanted from the precipitate deposited, and the latter washed with water, alcohol, etc., to remove the adsorbed salt or product of hydrolysis of the latter. The decanted solution and the wash-liquors are used instead of water for the peptization of a further quantity of cellulose. Instead of cooling and waiting for a precipitate to deposit, the mixture may be diluted with water, and the gelatinous cellulose separated by filtration. If a dispersoid (colloidal) solution is desired, the heating and addition of the salt are continued until the peptization is complete; from the colloidal solution, hydrated cellulose can be recovered in different forms by means of various coagulating agents. The hydrated cellulose prepared by this method, on account of its high degree of dispersion, is highly reactive. With certain salts, *e. g.*, sodium iodide, calcium bromide, iodide, and thiocyanate, strontium iodide and thiocyanate, barium thiocyanate, etc., the process can be carried out at atmospheric pressure, but with other salts, *e. g.*, sodium, potassium and barium chlorides, etc., increased pressure is necessary. With a concentrated solution of sodium chloride, peptization of cellulose begins at about 170° and 8 atmospheres pressure. In order to prevent decomposition of the cellulose, as far as possible, it is preferable to work at a moderate temperature and increase the solubility of the salt by increasing the pressure. With saturated solutions (at the boiling temperature under atmospheric pressure), peptization of cellulose proceeds rapidly with lithium chloride, bromide, iodide, and nitrate, sodium iodide, strontium iodide, and thiocyanate, calcium bromide, iodide, and thiocyanate, barium and manganese thiocyanates, etc. Soluinto solution when warmed to 100°, while the same salt in concentrated hydrochloric acid is reactive in the cold. Antimony pentachloride, tin tetrachloride and titanium tetrachloride mixed with a small amount of hydrochloric acid are also cellulose solvents. Cobalt chloride, auric chloride, uranyl chloride, cerous chloride and chromic chloride are less efficient. To secure a clear solution in such cases it is usually necessary to filter the liquid through an asbestos felt which has been washed with concentrated hydrochloric acid as portions of the filter remain dissolved. According to Deming the action of bromides in acid solution is complicated by the fact that hydrobromic acid has such a powerful effect on cellulose. The decomposition of the latter by hydrobromic acid gas in ethereal solution with the production of brommethylfurfural is known.[1] Concentrated aqueous hydrobromic acid dissolves cellulose almost instantly but, however, with profound decomposition. Aqueous zinc bromide exerts a dissolving action upon cellulose while the action is comparatively weak with zinc fluoride. Bismuth bromide and mercuric bromide dissolved in hydrochloric acid attack cellulose at concentrations where an equivalent amount of hydrobromic acid would disintegrate the fibers without dissolving them. The same is substantially true

tions of cellulose containing only about 1% of the latter set to transparent or semi-transparent jellies on cooling, and if the jellies are left exposed to the air, the salts effloresce, and a skeleton jelly of hydrated cellulose is left. With other salts, which effect peptization only on more prolonged heating, degradation of the cellulose to substances of lower molecular weight also takes place. Cellulose which has been swollen by soaking in concentrated saline solutions can be subsequently peptized much more readily than untreated cellulose.

[1] H. Fenton and M. Gostling, Proc. Chem. Soc. 1901, **17,** 119; J. C. S. 1901, **79,** 807; abst. Bull. Soc. Chim. 1901, **26,** 796; Rep. Chim. 1901, **1,** 424; Chem. Centr. 1901, II, 123, 426; Jahr. Chem. 1901, 838, 1494; Zts. ang. Chem. 1901, **14,** 273; Chem. Ztg. 1901, **25,** 180, 507. See also M. Gostling, J. C. S. 1903, **83,** 181; abst. J. Soc. Dyers Col. 1903, **19,** 69; Chem. Centr. 1903, I, 250, 629; Bull. Soc. Chim. 1903, **30,** 883; Rep. Chim. 1903, **3,** 224; Chem. Ztg. 1903, **27,** 102; Jahr. Chem. 1903, 1014. See also M. Conrad and M. Guthzeit; Ber. 1885, **18,** 439; 1886, **19,** 2659, 2844; abst. J. C. S. 1885, **48,** 745; 1887, **52,** 229; Bull. Soc. Chim. 1886, **46,** 10; 1887, **47,** 652; Jahr. Chem. 1885, 1745, 1746; Wag. Jahr. 1885, **31,** 753; 1886, **32,** 615. E. Winterstein (Zts. physiol. Chem. 1892, **17,** 400; abst. J. C. S. 1893, **64,** i, 127; Chem. Centr. 1893, I, 22; Jahr. Chem. 1892, 2475) has studied the action of dilute acids and alkalis upon cellulose prepared from various sources, and has expressed the loss sustained by the cellulose in a series of tables. The results obtained, in general, confirm the statements of previous observers that cellulose is but slightly attacked by very dilute, hot mineral acids. With alkalis (5%–10%) the cellulose is considerably dissolved, which is confirmatory of other investigators.

of zinc and mercuric iodides in HCl solutions which dissolve cellulose quite readily. Lead iodide and bismuth iodide, when dissolved in hydriodic acid cause cellulose to pass into solution, but the concentrated acid itself, it must be remembered, has considerable solvent power. The chlorides of the alkalis and alkaline earths will not dissolve cellulose in hydrochloric acid, one reason, perhaps, being the fact that the salts themselves are but sparingly soluble in the acid. However, solutions of calcium chloride, calcium bromide, barium bromide, magnesium bromide, lithium chloride and potassium chloride in formic acid or any mixture of the latter with hydrochloric acid do dissolve cellulose, a less decided action being obtained with solutions of lithium and calcium chlorides in trichloracetic acid.

Organic acids in solution, even when moderately concentrated, appear to have no injurious action upon cotton cellulose. Such non-volatile organic acids, however, as oxalic, tartaric and citric, when allowed to dry upon the fiber, act much in the same manner as an inorganic acid, especially at elevated temperatures. Acetic acid, however, exerts no destructive action, but cellulose previously soaked in acetic acid esterifies much more readily than if not so treated.[1]

E. Knecht[2] has shown that portions of calico printed with

[1] Chem. News, 1870, **21**, 144, 156; 1884, **49**, 190. C. Cross and E. Bevan, Chem. News, 1891, **63**, 66; abst. J. C. S. 1891, **60**, 890; Mon. Sci. 1892, **39**, 202; Chem. Centr. 1891, I, 534; Chem. Tech. Rep. 1891, I, 174; Chem. Ztg. Rep. 1891, **15**, 44; Jahr. Chem. 1891, 2181. T. Hanausek, Chem. Ztg. 1894, **18**, 441; Chem. News, 1894, **69**, 174, 192; abst. Chem. Centr. 1894, I, 864; Jahr. Chem. 1894, 1132. C. Cross and E. Bevan, Chemical Notes, Feb. 6, 1891; abst. Year Book Pharm. 1891, 91. F. and A. van den Bosch and O. Müller, E. P. 6942, 1906; abst. J. S. C. I. 1906, **35**, 775. Belg. P. 237056, 1911, Compagnie Francaise des Applications de la Cellulose.

[2] Seventh Intl. Cong. Appl. Chem. 1909; J. S. C. I. 1909, **28**, 700; abst. C. A. 1908, **2**, 3403; Zts. ang. Chem. 1909, **22**, 1120; Proc. Manch. Lit. Phil. Soc. 1908, **52**, II, XXII. A. Scheurer (Bull. Soc. Ind. Mulhouse, 1904, **74**, 211; abst. J. S. C. I. 1904, **23**, 981) has recorded some experiments, on the effect of oxalic, lactic, tartaric, citric, thiocyanic, *o*-, *m*-, and pyrophosphoric and phosphorous acids on cotton under the influence of dry and moist heats. Solutions of oxalic acid containing 10 and 20 gm. per liter were used, and solutions of the other acids of equivalent strength. Thiocyanic acid had the greatest effect on the tensile strength of the cotton in a dry atmosphere at 40°–50°, the stronger solution causing the tensile strength to fall to less than half its original value after 72 hours; the effect of thiocyanic to acid and steam is so small as to be negligible. Meta- and pyrophosphoric acids, in the stronger solutions, caused a reduction of about one-third of the tensile strength, both after three days of hot-air treatment and after one hour's steaming. The action of phosphorous and oxalic acids was somewhat less, the reduction being from 25% to 27% in either case. Lactic,

oxalic acid and thickened with "British gum," lose their characteristic properties—marked affinity for methylene blue and decreased affinity for direct colors—after boiling for a few minutes in dilute NaOH. No oxalic acid could be detected in the caustic soda extract, but formic acid was found, which appears to be formed by the decomposition of the oxalic acid, and to act upon the cellulose in the nascent state, forming formylcellulose. Malonic acid acts similarly, yielding cellulose acetate. No action was observed with succinic or glutaric acids.

Action of Salts on Cellulose. Under the topic "Solvents of Cellulose," it has been shown that by the action of concentrated neutral or acid aqueous solutions of salts at high temperatures upon cellulose, the latter may either be converted into a plastic or go entirely into solution. With less drastic treatment, as for example, the simple contact of cellulose with salt solutions, a certain affinity of the cellulose for various saline combinations has been noticed. In some instances the cellulose simply absorbs the salt from the solution, which can afterwards be removed by washing with water. In other cases the salt is fixed in the cellulose material and is not removed by simple washing with water. The results obtained by different workers, however, are not concordant.

Vignon[1] found one gram of cotton capable of retaining up to 0.4% of the salt from a solution containing 1 gm. ammonium chloride in 250 cc. water. He finds, however, that sodium chloride is not retained under similar conditions and this observation agrees with that of Mansier.[2] According to this worker, cellulose materials also retain calcium chloride. Against this latter assertion, we have the evidence of E. Knecht,[3] who states that

orthophosphoric, tartaric, and citric acids, in the order named, had still less effect on the tensile strength of the cotton, the reduction lying between 10% and 20%. The addition of glucose to the printing mixture containing oxalic acid diminished the destructive action of the acid under the influence of hot air or steam to a considerable extent, particularly in the former case.

T. Edison (Poly. Notiz. 1877, **32,** 352; Chem. Centr. 1877, **58,** 693; Chem. News, 1877, **36,** 138) has recorded that the vapor of chloral hydrate is a solvent of cellulose.

[1] See P. v. Weimar.

[2] Jour. Pharm. Chim. 1902, (6), **16,** 60; abst. Chem. Centr. 1902, II, 768, 769; J. C. S. 1902, **82,** ii, 690; J. S. C. I. 1902, **21,** 1098, 1155; Rep. Chim. 1902, **2,** 524; Jahr. Chem. 1902, 238; Zts. anal. Chem. 1904, **43,** 314.

[3] Ber. 1888, **21,** 1557, 2804; abst. Chem. Ztg. 1888, **13,** 1173; Chem. Ztg. Rep. 1888, **13,** 170; J. C. S. 1888, **54,** 832; J. S. C. I. 1888, **7,** 621; J.

no affinity is shown by cellulose for calcium chloride.

Various cellulose materials, such as cotton fiber, have the power of absorbing and fixing other salts, such as those of iron,[1] cerium,[2] copper,[3] lead,[4] and titanium.[5] It is considered[6] that a small quantity of oxycellulose or other cellulose derivatives may be responsible for the reactions recorded between cellulose materials and various metallic derivatives. The experiments of Molisch[7] tend to support this view, for he finds that cellulose after treatment with alkali, acquired increased affinity for the absorption and fixation of iron, lead and other metallic salts. He attributes the increased affinity not to the formation of oxycellulose, but rather to the presence of small quantities of pectic substances in the cellulose material.[8] The retention of salts in cellulose may be due not only to absorption and combination, but also in part to capillary action.[9]

In the above instances of the absorption and fixation of salts in cellulose we are dealing in the main with neutral salts. The phenomena must be regarded in a somewhat different light when

---

Soc. Dyers Col. 1888, 104; Bull. Soc. Chim. 1889, (3), **2**, 546; Mon. Sci. 1888, **32**, 1159; Chem. Ind. 1888, **11**, 400; Chem. Tech. Rep. 1888, II, 32; Jahr. Chem. 1888, 2865; Wag. Jahr. 1888, **34**, 1108; Zts. ang. Chem. 1888, **1**, 683; Tech. Chem. Jahr. 1888–1889, **11**, 234. See also Zts. Chem. Ind. 1887, 165; Wag. Jahr. 1887, **33**, 165.

[1] Schellen, Dissertation, Strassburg, 1905, 14.

[2] G. Witz, Bull. soc. ind. Rouen, 1882, 416; 1883, **11**, 169; abst. J. S. C. I. 1883, **2**, 378; Faerb. Must. Ztg. **17**, 129; Mon. Sci. 1883, **25**, 517; 1884, **26**, 1161; Jahr. Chem. 1883, 1782; Wag. Jahr. 1883, **29**, 1068; Dingl. Poly. 1883, **250**, 271. See also G. Witz, D. R. P. 24173. H. Schmid, Dingl. Poly. 1883, **250**, 272.

[3] Herzog, Zts. Farbenind. 1908, **1**, 281. v. Cochenhausen, Zts. ang. Chem. 1906, **19**, 1987, 2024; abst. Bull. Soc. Chim. 1907, (3), **37**, 491; Chem. Zentr. 1907, I, 188; Chem. Ztg. Rep. 1907, **31**, 11; Jahr. Chem. 1905–1908, I, 1397; Wag. Jahr. 1906, I, 539.

[4] E. Knecht, Jour. Soc. Dyers Col. 1909, **25**, 47. See also Frerichs, Apoth. Ztg. 1902, 884.

[5] Hibbert, Jour. Soc. Dyers Col. 1906, **22**, 278; Chem. Ztg. Repert. 1906, **30**, 394; C. A. 1907, **1**, 242; J. S. C. I. 1906, **25**, 880; Text. Col. **28**, 297.

[6] See Schwalbe, Die Chemie der Cellulose, 1911, 79–80.

[7] See W. Massot, Zts. ang. Chem. 1909, **22**, 241, 299; abst. C. A. 1910, **4**, 1240; Chem. Zentr. 1909, I, 801.

[8] Persoz, Traite de l'impression, 1846, **1**, 312.

[9] F. Goppelsroeder, "Darstellung der Farbstoffe," 1885. Zts. Chem. Ind. Koll. 1909, **4**, 94. See also R. Krulla, Zts. physik. Chem. 1909, **66**, 307; abst. Chem. Zentr. 1909, I, 1956; Jahr. Chem. 1909, 120; Meyer Jahr. Chem. 1909, **19**, 28; C. A. 1909, **3**, 1959; J. C. S. 1909, **96**, ii, 469; Bull. Soc. Chim. 1910, (4), **8**, 489; Rep. Chim. 1909, **9**, 387; Zts. Chim. Ind. Kol. 1909, **4**, 214; Chem. Tech. Rep. 1909, **33**, 325.

we consider the possibility of acid formation.[1] On this view, the neutral salt on heating would act in the same manner as an acid salt,[2] although possibly not so energetic.

Vignon has shown that a cellulose material such as cotton (which has received a preliminary alkali treatment), absorbs mercuric oxide with smaller quantities of mercuric chloride from a mercuric chloride bath. The mercuric chloride solution, in presence of cellulose under heat, appears to form mercuric oxide and hydrochloric acid[3] and the oxide remains combined with the cellulose. The absorption of mercuric chloride in smaller quantities has also been noted by W. Schellens.[4] Cellulose, which has first been soaked in a solution of aluminium sulfate or chloride and then dried, is stated on subsequent wetting, to show an acid reaction,[5] the cellulose fiber being attacked and weakened.[6] Possibly a basic salt is formed and free acid liberated. A similar formation of acid is stated to occur when the aluminium salt is replaced by certain other compounds such as magnesium chloride.[7] The fixing of metallic compounds is most marked in the case of salts which are readily dissociated. According to Girard[8] the main reaction consists in the transformation of cellulose into hydrocellulose by the action of acid. He considers that any carbonization occurring as a result of the dehydration is only an

---

1. J. Barral and Salvetat, Ann. Chim. Phys. 1876, (5), **9**, 127; Compt. rend. 1875, **81**, 1189; abst. Chem. News, 1876, **33**, 18; J. C. S. 1876, **30**, i, 821; Bull. Soc. Chim. 1876, **25**, 425; Mon. Sci. 1876, **18**, 90; Ber. 1876, **9**, A, 68; Dingl. Poly. 1876, **219**, 469; Jahr. Chem. 1875, 1164. See also Bayer Ind. Gew. 1875, 296; abst. Dingl. Poly. 1876, **219**, 182.
2. R. Schwarz, Faerb. Ztg. 1908, **19**, 66, 87; abst. C. A. 1908, **2**, 2158; J. S. C. I. 1908, **27**, 329; Rep. Chim. 1908, **8**, 280; Chem. Zentr. 1908, I, 1502; Zts. ang. Chem. 1908, **21**, 2480.
3. Vignon, Compt. rend. 1893, **116**, 517, 584, 645; Bull. Soc. Chim. 1893, (3), **9**, 502, 506; abst. Chem. News, 1893, **68**, 49; J. C. S. 1893, **64**, i, 387; J. S. C. I. 1893, **12**, 948; Chem. Centr. 1893, **64**, I, 708, 844; Chem. Ztg. 1893, **17**, 74; Chem. Ztg. Rep. 1893, **17**, 97; Jahr. Chem. 1893, **47**, 882. See also Compt. rend. 1890, **110**, 534; abst. Chem. News, 1893, **67**, 145; Bull. Soc. Chim. 1890, (3), **3**, 405, 472, 851; 1891, (3), **5**, 557; Chem. Ztg. Rep. 1890, **14**, 55; 1891, **15**, 76, 111.
4. Arch. Pharm. 1906, **243**, 617; abst. Jahr. Chem. 1905–1908, II, 3183. Blondel, Zts. Farbenind. 1904, **3**, 291. F. Breinl and C. Hanofsky, Gewerbemus. 1892, 203; Chem. Ztg. 1897, **21**, 563.
5. Liechti and Suida, Gewerbemus. 1883.
6. Kielmayer, Faerberlehrling, 133.
7. E. Uhler, Faerb. Ztg. 1908, **57**, 1; abst. Chem. Ztg. Repert. 1908, 32, 44; C. A. 1908, **2**, 1048.
8. Ann. Chim. Phys. 1881, (5), **24**, 333; abst. Ber. 1881, **14**, II, 2834; Jahr. Chem. 1881, **34**, 985; J. C. S. 1882, **42**, 378; Proc. U. S. Nav. Inst. 1882, **8**, 209; Bull. d'Enc. **81**, 176; Bull. Musee. **82**, 80; Naturforscher, **15**, 26.

accompanying factor, though other workers[1] contend that dehydration is the main factor. The weakening of the fiber may be also due to a catalytic transference of oxygen by the salts or the oxides separated.[2] Iron, copper, and possibly aluminium oxide act as oxygen carriers.[3]

Kolb[4] accounts for the weakening of cellulose which occurs when the cellulose fiber has been moistened with a salt solution and then dried at a high temperature in a different manner. He considers the weakening as brought about by a mechanical process, and infers that crystals in the dried material actually cut the fibers. With neutral salts such as sodium sulfate he finds weakening of the fiber of the cellulose material. These observations indicate that the formation of acid does not always account for carbonization. Against the acid formation theory the evidence of Chevreul[5] is important. He has shown that a piece of woollen fabric containing cellulose, when saturated with an amount of hydrochloric acid corresponding to a given quantity of aluminium chloride, does not show destruction on heating. No hydrochloric acid vapors are detected on heating to 140° a cellulose which has been previously soaked in ammonium chloride solution.[6] Moreover, when aluminium chloride is employed the color of the wool is not changed, while with free hydrochloric acid the

1. See C. Beadle, La papeterie, 1909, **31**, 69.

2. P. Sisley, Rev. mat. Col. 1909, **13**, 8; abst. C. A. 1909, **3**, 1692; Rep. Chim. 1909, **9**, 280; Bull. Soc. Chim. 1909, (4), **5**, 1; J. S. C. I. 1909, **28**, 136.

3. Witz, Bull. soc. ind. Rouen, 1883, **11**, 212.

4. J. Kolb, Bull. Mulhouse, 1868, **38**, 920; Compt. rend. 1868, **66**, 1024; **67**, 742; Instit. 1868, 329; Ann. Chim. Phys. 1868, (4), **14**, 348; Bull. Soc. Chim. 1869, (2), **11**, 431; Dingl. Poly. 1845, **95**, 62; **96**, 321; Jahr. Chem. 1868, **21**, 981.

5. Compare R. Buntrock and E. Raeuber, Text. u. Faerb. Ztg. 1903, 3, 21, 123; abst. Jahr. Chem. 1903, **56**, 1560. T. Appleyard and T. Deakin, J. Soc. Dyers Col. 1902, **18**, 128; Rev. mat. color. 1902, **6**, 166; J. S. C. I. 1902, **21**, 702. R. Schiller and R. Bauer, D. R. P. 212694; abst. Wag. Jahr. 1909, II, 465; Zts. ang. Chem. 1909, **22**, 861. U. S. P. 917402, 1909; abst. J. S. C. I. 1909, **28**, 471. L. Cassella & Co., Zts. ang. Chem. 1909, **22**, 88, 1861; Oest. Woll. Leinenind. 1909, **29**, 520.

6. A. Beck, Bull. soc. ind. Rouen, 1904, **32**, 351; Zts. Farbenind. 1905, **4**, 49; Chem. Ztg. Rep. 1904, **28**, 707. G. de Keukelaere, D. R. P. 169448; Faerb. Ztg. 1906, **17**, 261; Chem. Ztg. 1906, **30**, 405; Wag. Jahr. 1906, **52**, II, 398; Zts. ang. Chem. 1906, **19**, 1815. B. Rassow (Zts. ang. Chem. 1911, **24**, 1127; J. S. C. I. 1911, **30**, 1307; C. A. 1912, **6**, 684) has examined the capacity of cellulose for absorbing and fixing small quantities of metal from dilute solutions of copper, nickel, aluminium and potassium salts.

color is destroyed. A basic aluminium salt is probably precipitated which protects the color. The type of material employed may influence the result obtained and in part explain the apparently contradictory results of various workers. Thus, according to Breinl and Hanofsky,[1] cellulose (e. g., filter paper), which has been soaked in aluminium chloride and then dried at a high temperature, evolves hydrochloric acid in small quantities. In a comparative experiment using sheep-wool instead of cotton, practically no hydrochloric acid was evolved. Sisley,[2] on heating various cellulose materials at a high temperature with sodium chloride, finds that cotton acts in an entirely different manner to silk and wool.

L. Liechti and W. Suida have shown in their investigation with aluminium salts,[3] that the fact that a salt is basic is no indication that it possesses powers of mordanting, the basic chlorides and oxychlorides of aluminium not being mordants.

R. Haller[4] has studied the behavior of cotton of different degrees of purification towards solutions of metallic salts. Representative samples of Indian, American and Egyptian cotton were prepared in different stages of chemical purification following the usual industrial bleaching process. The samples were treated at the ordinary temperature for 48 hours with solutions of aluminium sulfate, aluminium acetate, and lead acetate. The change in the percentage of metallic base in the solutions was then determined in order to have an approximate measure of the absorption, and the quantity of metallic base fixed by the cotton after washing was determined

[1] F. Breinl and C. Hanofsky, Gewerbemus. 1892, 203; abst. Chem. Ztg. 1897, **21**, 563. See P. Bolley, Ann. 1859, **106**, 235; Kritische und experimentelle Beitraege zur Theorie der Faerberei, Zurich, 1859; Dingl. Poly. 1859, **153**, 362, 431; Phil. Mag. 1859, (4), **18**, 481; Chem. Centr. 1859, **30**, 897; N. Arch. phys. nat. **6**, 67. J. Boeseken, G. Tergau and A. Binnendijk, Proc. Acad. Sci. Amsterdam, 1919, **21**, 893; abst. C. A. 1919, **13**, 2123.

[2] Rev. Mat. color. 1909, **13**, 9; abst. C. A. 1909, **3**, 1692; Rep. Chim. 1909, **9**, 280; Bull. Soc. Chim. 1909, (4), **5**, 1; J. S. C. I. 1909, **28**, 136. Moehlau, Ber. 1886, **19**, 2914; abst. J. C. S. 1886, **50**, 947; J. S. C. I. 1886, **5**, 597; Bull. Soc. Chim. 1886, (2), **46**, 121; Chem. Ind. 1886, **9**, 254; Jahr. Chem. 1886; **39**, 2201; Wag. Jahr. 1886, **32**, 508. Green and R. Levy, Rev. mat. color. 1897, **1**, 378; 1898, **2**, 28; abst. Meyer Jahr. Chem. 1897, **7**, 473.

[3] J. S. C. I. 1883, **2**, 537; J. C. S. 1884, **46**, 794; Chem. Ind. 1884, **7**, 129; Dingl. Poly. 1884, **251**, 177; Jahr. Chem. 1883, **36**, 1784; Wag. Jahr. 1883, **29**, 1078; Mittheil des techn. Dewer. Wien. 1883, No. 1, 3.

[4] Chem. Ztg. 1918, **42**, 597; abst. J. S. C. I. 1919, **38**, 70-A.

by incineration. In some cases with aluminium sulfate and in all cases with aluminium acetate, a negative absorption was observed, that is, the concentration of metallic base in solution was increased instead of decreased by the action of the cotton. Using aluminium acetate, the negative absorption was smallest in the case of the raw fiber and became greater as the degree of purification was increased. Cotton which had been boiled with lime gave higher values than that which had been boiled with caustic soda. Negative adsorption was most pronounced in the case of the Egyptian cotton. Using aluminium sulfate, positive adsorption was observed in all cases with the raw cotton and with those which had been boiled with lime; on the other hand, the samples boiled with caustic soda, also those boiled first with lime and then with soda, and the fully bleached samples, all showed negative adsorption, increasing generally with the degree of purification.

Lead acetate showed in all cases a large positive adsorption increasing with the purification of cotton. The maximum adsorption in all cases, both positive and negative, appears to correspond with maximum purification of the cotton, which is attained by boiling first with lime and then with caustic soda, with a sour after each boil. Treatment with bleach liquor appears to decrease the purity of the cellulose, at least it lowers the adsorption values. An exceptionally large adsorption with lead acetate was shown by the raw cottons; no doubt, the ease of wetting by the various solutions plays a part. Adsorption does not necessarily run parallel with fixation of insoluble base in the fiber. In all the experiments with aluminium salts, there was a fixation of alumina, even when negative adsorption values were recorded. In the experiments with lead acetate showing high positive adsorption, a large fixation was at the same time observed in the case of the raw cottons, and the appearance suggested that the lead oxide was combined with some of the non-cellulose constituents. After boiling, the amount of fixation of lead oxide became smaller with increasing purification of the cotton, although the adsorption became more marked.

Cellulose and Acids. Comparatively early in the development of cellulose, it was recognized that even the action of diluted inorganic acids tended to diminish the strength of the cellulose. The destruction of the cotton in half-woollen rags by means of saturation and subsequently heating with acids is said to have been first practiced in England by G. Koeber in 1852, while the removal of extraneous material from wool by the same means is supposed to have been originated in 1854 by Isart and Frezon. R. Fenton is said to have patented this idea of Koeber in 1853.[1] It was in 1868 that J. Kolb observed[2] that when a sample of linen yarn is immersed in sulfuric acid of 4° Bé. strength for 25 hours its strength is reduced from 1.25 to 0.68 kilos, and emphasized the fact that even very diluted acids must not be allowed to dry on the material.

When J. Barral and Salvetat[3] treated cotton cellulose with 5% solution of hydrochloric, nitric and boric acids at 140°, the cellulose darkened and could readily be rubbed to a powder. These results were confirmed and extended by A. Girard in 1875,[4] who described the preparation of a structureless cellulose of greatly diminished tensile strength by immersion of cotton in 55% sulfuric acid for 12 hours. His analyses indicated a water-absorption conforming to the formula, $C_{12}H_{22}O_{11}$. He[5] proposed for this product the name "hydrocellulose," this modification representing, in his judgment, the first stage in the breaking down of the cellulose molecule to glucose, and saw in parchment, a paper glued together by the superficial formation of this hydrocellulose. He distinguished two forms of cellulose, one which preserved the morphological structure of the cotton filament, and the other, which is gelatinous and without structural form, being easily reduced to a pulverulent state by rubbing. The properties of hydrocellulose are detailed more extensively under the topic "Hydrocellulose," but in connection with the tendering of cellulose by means of acids, the fact must be remembered that be-

---

[1] E. P. 1891, 1853.

[2] Bull. Mulhouse, 1868, **38**, 922.

[3] Ann. Chim. Phys. 1876, (5), **9**, 129; abst. Chem. News, 1876, **33**, 18; J. C. S. 1876, **29**, 821; Bull. Soc. Chim. 1876, **25**, 425; Compt. rend. 1875, **81**, 1189; Mon. Sci. 1876, **18**, 90; Ber. 1876, **9**, 68; Dingl. Poly. 1876, **219**, 469; Jahr. Chem. 1875, 1164.

[4] Compt. rend. 1875, **81**, 1105; 1879, **88**, 1322; **89**, 170; Ann. Chim. Phys. 1881, (5), **24**, 337; abst. J. C. S. 1879, **36**, 911; 1882, **42**, 378; Jahr. Chem. 1875, 786; 1879, 835; 1881, 985; Proc. U. S. Nav. Inst. 1882, **8**, 309; Ber. 1879, **12**, 2158; 1881, **14**, 2834; Wag. Jahr. 1879, **25**, 419; Bull. Soc. Chim. 1880, **34**, 507; Mon. Sci. 1879, **21**, 958; Chem. News, 1881, **44**, 216; J. A. C. S. 1879, **1**, 400; Jahr. rein Chem. 1875, 142; 1881, 460.

[5] Ann. Chim. Phys. 1876, (5), **9**, 116.

sides a loss of strength, comes at the same time an increased affinity of the cellulose for basic dyestuffs.

This characteristic property of loss of strength and increased attraction for dyestuffs, when cellulose is treated with acids has been the subject of numerous investigations right down to the present time, as the phenomena exhibited is of paramount importance in several branches of the textile art.

L. Vignon[1] has made comparative examinations of the absorption of acids by cotton, wool and silk, the values found for cotton being reproduced below. They are of interest in connection with the subsequent development of the cellulose ester art in indicating how the preliminary treatment of the cellulose may so affect its structure and composition as to be reflected in variations in solubility and stability when the cellulose is afterwards nitrated, acetated or alkylated.[2]

TABLE VII.—ACTION OF SULFURIC ACID ON COTTON

Kind of Fiber	400 gm. Acid 1%.				
	Weight	K	K_1	K_2	K_1/K_2
Crude silk	10.00	1.015	0.959	2.169	2.26
Dressed silk	8.63	1.015	0.985	1.379	1.40
Cotton	9.12	1.015	1.016	.....	....
Wool	9.85	1.015	0.902	4.379	4.85
	400 gm. Acid 0.1%.				
	Weight	K	K_1	K_2	K_1/K_2
Crude silk	9.92	0.098	0.054	1.77	32.77
Dressed silk	10.30	0.098	0.070	1.06	14.93
Cotton	9.13	0.098	0.095	.....	.....
Wool	9.70	0.098	0.026	2.90	111.5

---

[1] Compt. rend. 1906, **143**, 550; Rev. mat. color, 1907, **11**, 15; Bull. Soc. Ind. Mulhouse, 1906, **76**, 359; Bull. Soc. Chim. 1906, **35**, 1140; Zts. ang. Chem. 1907, **20**, 1144; C. A. 1907, **1**, 781; J. C. S. 1907, **92**, i, 102; J. S. C. I. 1906, **25**, 1038; 1907, **26**, 195; Rep. Chim. 1907, **7**, 91; Chem. Centr. 1906, II, 1852; 1907, I, 517; Jahr. Chem. 1905–1908, II, 3181; Chem. Ztg. 1906, **30**, 1078, 1263.

[2] In the above table, which is taken from Schwalbe, "Die Chemie der Cellulose," 43, K signifies the weight in gm. of the acid in 100 gm. of solution before the experiment; K_1 the weight in gm. after the experiment; K_2 is the weight in gm. of acid fixed upon 100 gm. cotton, not including the acid soaked up. The hanks were immersed for one hour at ordinary temperature in 1% and 0.1% solutions of H_2SO_4. The cotton was thoroughly washed with distilled water before the experiment.

L. Vignon has likewise shown[1] that the acid absorption is also accompanied by a certain and definite evolution of heat, the calories evolved by immersing cotton in a normal solution of acid being shown in the following table:

TABLE VIII.—COTTON

	Spun, Unbleached		Loose, Bleached	
	For 100 gm.	For 1 mol.	For 100 gm.	For 1 mol.
H_2SO_4.....	0.40	0.65	0.40	0.65
HCl.......	0.38	0.60	0.36	0.58

E. Blondel[2] found that sulfuric acid of 55%–62% slowly changes cellulose at ordinary temperature, so that methylene blue produces deep shades—a characteristic of oxycellulose—the conditions of treatment being practically the same as that described by A. Girard for the preparation of hydrocellulose.

According to E. Grandmougin[3] very dark shades are produced by dyeing those spots which previously have been touched with 5% sulfuric acid, and this is borne out by the results of C. Koechlin.[4] The data obtained by Vetillart is not so conclusive.[5]

It has been found that sodium sulfate exerts a neutralizing action on the acid with less resultant tendering of cotton, due in all probability to the formation of acid sodium sulfate. Later it was found that with oxalic acid, sodium acid oxalate is the main product of the reaction between oxalic acid and sodium sulfate. M. Fort and F. Pickles[6] have applied some of the modern views of physical chemistry obtained from electric conductivity experiments with solutions of acids and salts to the tender-

---

[1] Compt. rend. 1890, **110**, 286, 909; Bull. Soc. Chim. 1890, **3**, 405, 851; abst. J. C. S. 1890, **58**, 553, 939; J. S. C. I. 1890, **9**, 855; Mon. Sci. 1890, **35**, 412, 635; Ber. 1890, **23**, R, 555; Chem. Centr. 1890, I, 591, 988; Jahr. Chem. 1890, 272, 273; Wag. Jahr. 1890, **36**, 1122; Zts. ang. Chem. 1890, **3**, 278.

[2] Bull. soc. ind. Rouen, 1882, **10**, 438, 471.

[3] Zts. Farbenind. 1907, **6**, 2; abst. Chem. Zentr. 1907, I, 946; Chem. Ztg. Rep. 1907, **31**, 77; Meyer Jahr. Chem. 1907, **17**, 504.

[4] Bull. Soc. Ind. Mulhouse, 1888, **55**, 547; Mon. Sci. 1888, **31**, 509, 1385; Chem. Ind. 1888, **11**, 400; 1889, **12**, 15; Chem. Tech. Rep. 1888, I, 37, 71; II, 60; Chem. Ztg. 1888, **12**, 375; Jahr. Chem. 1888, 2859.

[5] Bull. soc. ind. Rouen, 1883, **11**, 234.

[6] J. Soc. Dyers Col. 1915, **31**, 255; abst. C. A. 1916, **10**, 2527; J. S. C. I. 1916, **35**, 38.

ing of cotton, their results being expressed in a series of tables. One table gives relative strengths of acids used and their inverting efficiency for comparison with tendering results with sulfuric, hydrochloric, acetic, phosphoric, trichloracetic and tartaric acids and acid sodium sulfate. Their method was to treat 5 gm. samples of cotton cellulose with 100 cc. of a solution of a definite normality under a reflux condenser at a temperature maintained by a boiling water-bath.

They found that the tendering action (hydrolysis) of acids on cellulose, like the inversion (hydrolysis) of cane sugar, is dependent on the strength or electric conductivity of the acid. The extent of tendering varied with the strength of the acid used except in the case of trichloracetic acid, which decomposes into HCl and glycollic acid on boiling with water. In experiments with sodium chloride, sulfate, oxalate or acetate or with zinc or magnesium chlorides or magnesium sulfate, no considerable degree of tendering was caused except by $NaHSO_4$. Tendering was increased by the addition of magnesium sulfate, probably by the liberation of HCl. It was also noted that the elongation figures are considerably effected in which the tensile strength is not.[1]

H. Wilkinson has found[2] that cellulose fibers treated with aqueous sulfuric acid and dried without heat, although tendered when in the acidified condition apparently regained somewhat in strength on neutralization of the acid. Tensile strength tests indicated:

1. Tendering action increases with length of time the acid

---

[1] From their results the following conclusions may be drawn: (1) The addition of a salt of the same acid to a solution of an acid causes reduced electrolytic dissociation of the acid, and also causes a corresponding reduction in the tendering action on cotton. (2) The addition of a salt of a weaker acid to the solution of an acid, produces a large amount of weak, feebly ionized acid which replaces the strong, highly ionized acid, also results in a decreased tendering action upon cellulose. (3) The addition of a salt of a stronger acid to the acid solution sets up an equilibrium whereby the total acid effect (measured by electric conductivity) becomes greater and results in an increased tendering action, depending upon how much of the stronger acid is required to be set free to acquire equilibrium. (4) The results of Pilkington that oxalic, citric and tartaric acids all tender less when padded and steamed in the presence of sodium sulfate was confirmed also for the treatment of cotton with a hot solution of oxalic acid, the sodium acid oxalate formed being separated and analyzed.

[2] J. Soc. Dyers Col. 1917, **33**, 148; abst. C. A. 1918, **12**, 1254; J. S. C. I. 1917, **36**, 707.

remains on the fiber, and is greatly accelerated by heat.

2. Cotton regained in strength considerably on washing out the acid, gain being less in those samples which had been tendered greatest in the acidified condition.

3. Neutralization by alkali and then washing, gave same results as those obtained by washing only.

The action of diluted sulfuric acid upon cellulose has been studied by A. Scheurer[1] and C. Koechlin,[2] who found appreciable weakening of the fiber when the concentration of the acid was 0.2% at 80° for 30 minutes, and especially after one hour's immersion. E. Knecht,[3] as the result of boiling cotton cellulose with dilute sulfuric acid, was unable to determine whether the acid was bound physically or chemically. According to Kuehn[4] and Aronstein and Schulze,[5] on boiling cellulose with 5% H_2SO_4 but 0.64% sugar (calculated on the cellulose) was formed. Kern[6] found the action to be much more pronounced when the cellulose had previously been boiled with 1.25% KOH solution. In general the results obtained in this direction have been insufficiently investigated in a quantitative direction, in that, in the majority of instances, no determinations were made of the changes in the dissolved portion, only the amount of sugar formed being estimated.

On boiling with 50% sulfuric acid, C. Cross, E. Bevan and C. Smith[7] observed the formation of the following products:

---

[1] Bull. Soc. Ind. Mulhouse, 1888, **55**, 364, 399, 439; abst. Mon. Sci. 1889, **33**, 257; J. S. C. I. 1888, **7**, 841, 843; Jahr. Chem. 1889, 2841; Chem. Tech. Rep. 1888, II, 60, 105; Chem. Ind. 1889, **12**, 40; Wag. Jahr. 1888, **34**, 1099; Bull. Soc. Chim. 1888, **50**, 597.

[2] Bull. Soc. Ind. Mulhouse, 1888, **55**, 547; abst. Mon. Sci. 1888, **31**, 509, 1385; Chem. Ind. 1888, **11**, 400; 1889, **12**, 15; Chem. Tech. Rep. 1888, I, 37, 71; II, 60; Chem. Ztg. 1888, **12**, 375; Jahr. Chem. 1888, 2859.

[3] J. Soc. Dyers Col. 1888, **4**, 104; abst. J. S. C. I. 1888, **7**, 621; Bull. Soc. Chim. 1889, **2**, 846; Mon. Sci. 1888, **31**, 1459; Ber. 1888, **21**, R, 708; Chem. Ind. 1888, **11**, 552; Chem. Tech. Rep. 1888, II, 101; Chem. Ztg. 1888, **12**, 1173; Jahr. Chem. 1888, 2864. See also E. Mills and J. Takamine, J. C. S. 1883, **43**, 142; abst. Chem. News, 1882, **46**, 299; Ber. 1883, **16**, 973; Jahr. Chem. 1883, 1784. E. Knecht (Seventh Intl. Cong. Appl. Chem. 1909; J. S. C. I. 1909, **28**, 700; Proc. Manch. Lit. Phil. Soc. 1908, **52**, II, XXII; abst. C. A. 1908, **2**, 3403; Zts. ang. Chem. 1909, **22**, 1120) has also studied the action of oxalic acid on cellulose.

[4] J. Landw. 1865, 304.

[5] Zts. physiol. Chem. 1890, **14**, 244.

[6] Jour. Landw. 1876, 19; Zts. physiol. Chem. 1890, **14**, 244.

[7] Ber. 1895, **28**, 1943; abst. J. C. S. 1895, **68**, i, 640; Chem. Centr. 1895, II, 832; Jahr. Chem. 1895, 1350.

Material Taken	Furfurol	Acetic Acid	Formic Acid
Swedish filter paper........	0.3%	2.7%	17.2%
Bleached cotton...........	Trace	3.1%	13.2%
American crude cotton.....	......	5.0%	9.4%

Of the action of sulfurous acid, little definite is known. A Girard[1] ascribed the friability of fabrics saturated with solutions of sulfur dioxide to be due to the action of sulfuric acid formed by the oxidation of the SO_2 in the presence of water.

Although a weak acid, hydrogen sulfide under certain conditions exercise a vigorous action upon cellulose. Dumas has shown that in a wet fabric saturated with H_2S, at 40°, sulfuric acid was formed by atmospheric oxidation.[2]

Acid Celluloses. As referred to under the topic "Oxycellulose," G. Bumcke and R. Wollfenstein[3] have shown that our knowledge of cellulose is primarily based upon the ease with which it changes into dextrin and glucose, intermediate derivatives in this process of degradation being hydrocellulose and oxycellulose. The contention of G. Bumcke and R. Wollfenstein as the result of their repeating the work of G. Witz,[4] H. Schmid,[5] P. Richard,[6] L. Vignon[7] and A. Nastukoff,[8] is that insufficient proof has been

1. Ann. Chim. Phys. 1881, (5), **24,** 337; Compt. rend. 1877, **81,** 1105; 1879, **88,** 1322; **89,** 170; Bull. Soc. Chim. 1880, **34,** 507; abst. Mon. Sci. 1879, **21,** 958; J. C. S. 1879, **36,** 911; 1882, **42,** 378; Wag. Jahr. 1879, **25,** 419; Ber. 1879, **12,** 2158; 1881, **14,** 2834; Chem. News, 1881, **44,** 216; J. A. C. S. 1879, **1,** 400; Proc. U. S. Nav. Inst. 1882, **8,** 309; Jahr. Chem. 1875, 786; 1879, 835, 1116; 1881, 985; Jahr. rein Chem. 1875, 142; 1881, 460.

2. Compt. rend. 1846, **23,** 774; Instit. No. 669, 357; abst. Berz. Jahr. 1848, **27,** 42; Annuaire de Chim. 1847, 797.

3. Ber. 1899, **32,** 2493; abst. J. C. S. 1899, **76,** i, 852; J. S. C. I. 1899, **18,** 940; Bull. Soc. Chim. 1900, **24,** 620; Chem. Centr. 1899, II, 752; Jahr. Chem. 1899, 1290; Meyer Jahr. Chem. 1899, **9,** 300.

4. Bull. soc. ind. Rouen, 1882, 416; 1883, 169; abst. Wag. Jahr. 1883, **29,** 1068; Mon. Sci. 1884, **26,** 1161; see also H. Schmid, Dingl. Poly. 1883, **250,** 271; abst. J. C. S. 1884, **46,** 528.

5. Wag. Jahr. 1883, **29,** 1076.

6. Wag. Jahr. 1883, **29,** 1112.

7. Compt. rend. 1897, **125,** 448; Bull. Soc. Chim. 1898, **19,** 790; abst. J. C. S. 1898, **74,** i, 8; J. S. C. I. 1897, **16,** 908; Rev. Phys. Chim. 1897–1898, **2,** 21; Mon. Sci. 1897, **49,** 859; Chem. Centr. 1897, II, 843; Chem. Ztg. 1897, **21,** 811; Jahr. Chem. 1897, 1506. Compt. rend. 1898, **126,** 1355, 1658; **127,** 872; abst. J. C. S. 1898, **74,** i, 620; J. S. C. I. 1898, **17,** 680; Bull. Soc. Chim. 1898, **19,** 810; Mon. Sci. 1898, **51,** 454; Rev. gén. sci. 1898, **9,** 918; Chem. Centr. 1898, II, 24, 972; Chem. Ztg. 1898, **22,** 425; Jahr. Chem. 1898, 2265.

8. J. Russ. Phys. Chem. Soc. 1892, **24,** 256; Bull. Soc. Ind. Mulhouse, 1892, 493; abst. J. C. S. 1893, **64,** i, 387; J. S. C. I. 1893, **12,** 516; Bull. Soc. Chim. 1893, **10,** 124; Ber. 1892, **25,** R, 911; Chem. Ztg. Rep. 1892, **16,** 293; Meyer Jahr. Chem. 1893, **3,** 517; Wag. Jahr. 1892, **38,** 989.

adduced for the homogeneity of the celluloses operated upon, while the oxycelluloses produced by different processes, and by modifying the same process, are not always identical. While there is practically no contention as to the direct entry of oxygen into the cellulose molecule in the formation of the oxycelluloses, the mechanics of the reaction is invariably complicated by the presence of hydrolyzing processes. The "hydralcellulose" of these investigators is transformed by boiling with ten times its weight of 10% aqueous NaOH into roughly two-thirds cellulose, and one-third acid cellulose, this latter body being readily precipitated from the alkaline solution by acids.

The same phenomenon occurs when hydralcellulose is allowed to stand in the cold for some time with sodium hydroxide. Acid cellulose is distinguished from cellulose by its solubility when freshly prepared in NaOH solutions, and from hydralcellulose by the absence of aldehydic properties. Acid cellulose dissolves in concentrated HCl, from which it may be recovered unaltered from the acid solution by dilution with water or by the addition of alkalis to neutralization.

When a HCl solution of acid cellulose is allowed to stand for some time, or upon heating, it loses the property of precipitation upon dilution with water. From the fact that the solution strongly reduces Fehling's solution it is evident that hydrolysis has taken place, and this occurs more readily in acid solution than does ordinary cellulose. The solubility in NaOH is lost by acid cellulose upon drying, as well as its property of hydrolysis in the presence of concentrated HCl. Dry acid cellulose appears as a light greenish, brittle but exceedingly hard mass, translucent like horn, and pulverizable with difficulty. When subjected to analysis, 3.05% ash was found, and combustion gave figures leading to the formula $C_{36}H_{60}O_{31}$ for the dry, and $C_{36}H_{62}O_{32}$ for the moist acid cellulose.

C. Haeussermann[1] does not agree that acid cellulose contains carboxyl groups, and calls attention to similar products obtained

---

[1] Zts. Schiess Spreng. 1906, **1**, 305; abst. Chem. Centr. 1906, II, 1830; Jahr. Chem. 1905–1908, II, 980; Meyer Jahr. Chem. 1906, **16**, 324. See also M. Hoenig and S. Schubert, Wien. Akad. Ber. 1885, **92**, II, 737; Monatsh. 1885, **6**, 708; 1886, **7**, 455; abst. J. C. S. 1886, **50**, 44; 1887, **52**, 125; Bull. Soc. Chim. 1886, **46**, 517; 1887, **47**, 578; Ber. 1885, **18**, R, 614; 1886, **19**, R, 748; Chem. Tech. Rep. 1886, II, 218; Jahr. Chem. 1885, 1575; 1886, 1780; Wag. Jahr. 1886, **32**, 610.

from the cellulose nitrates. He is opposed to the assumption of an acid character to the acid celluloses on account of its indifference in the moist state to ammonia, alkaline carbonates, lime and baryta water, and also on account of the fact that upon attempting dialysis in pure water, coagulation almost immediately occurs. Acid cellulose differs from the β-oxycellulose of Cross and Bevan by its insolubility in ammonia, and is not identical with the oxycellulose of Nastukoff, which is converted into water-soluble compounds by treatment with dilute sulfuric acid, followed by treatment with dilute alkali. Haeussermann holds that acid cellulose is also formed by the saponification of those particular nitrocelluloses which form upon treatment of cotton by cold nitric acid of 1.473 sp. gr. As yet, acid cellulose has not been prepared free from ash, the air-dry product, even after repeated washing, showing 2%–2.5% of ash. Haeussermann has shown that in the denitration of nitrocellulose filaments, the cellulose formed is, at ordinary temperatures more or less soluble in 10% NaOH solution and in concentrated HCl, and upon the precipitation of such a solution by dilution with water a flocculent coagulum is obtained which is completely dissolved in 10% sodium hydroxide solution, this being in contradistinction to the precipitation of cellulose from a cuprammonium solution by HCl, which gives a product insoluble in alkalis.

According to C. Schwalbe,[1] apparently the same acid cellulose is formed when cellulose is placed in a dish and 30% aqueous NaOH poured over it and subsequently heated to boiling. After boiling and decanting the supernatant solution and repeating this process several times, a clear solution results, thus indicating that cellulose can be completely hydrolyzed.

Bumcke and Wollfenstein do not regard the formation of acid cellulose as an oxidation process, but rather the cellulose as being first hydrolyzed to hydralcellulose, and this in turn forms acid cellulose under the influence of the alkali. They regard the product recovered from cuprammonium cellulose solutions as similar to acid cellulose, the slight reducing property being as-

---

[1] Chemie der Cellulose, p. 204. W. Hoffmeister, Landw. Versuchstat. 1891, **39**, 461; abst. J. C. S. 1892, **62**, 129; J. S. C. I. 1892, **11**, 452; Ber. 1893, **26**, R, 497; Chem. Centr. 1892, I, 27; Chem. Ztg. Rep. 1891, **15**, 317; Jahr. Chem. 1891, 2180; Wag. Jahr. 1891, **37**, 1105; Zts. ang. Chem. 1891, **4**, 709.

cribed to the presence of small amounts of hydralcellulose. H. Ditz[1] has described a supposed acid cellulose obtained by him by the oxidation of cellulose with ammonium persulfate.

Eckstroem[2] has obtained patent protection for the conversion of wood waste into sugar, in which he assumes an acid cellulose to be formed among the products of the degradation of cellulose to sugar. He assumes the acid cellulose to be first formed, which is then converted into dextrin and finally into grape sugar.

Eckstroem treats the wood waste or other form of cellulose with 70% sulfuric acid at 10°–40° for about 20 minutes, when the cellulose becomes converted into a thick jelly-like mass which is alleged to be a homogenous substance of acid reaction and containing carboxyl groups, and not to possess aldehydic properties. On boiling with water a small portion is transformed into grape sugar, but when boiled with acids, this conversion is complete.

Amyloid.[3] According to E. Winterstein, amyloid is a con-

[1] Chem. Ztg. 1907, **31**, 833, 844, 857; abst. C. A. 1907, **1**, 2941; J. C. S. 1907, **92**, i, 129; J. S. C. I. 1907, **26**, 988, 1026; Bull. Soc. Chim. 1907, (4), **2**, 1468; Chem. Zentr. 1907, II, 1606; Jahr. Chem. 1905–1908, II, 964; Meyer Jahr. Chem. 1907, **17**, 504; Wag. Jahr. 1907, II, 507; Zts. ang. Chem. 1908, **21**, 1185. For the G. Fink method for the production of acid derivatives of cellulose, see D. R. P. Anm. F-29131, F-32918; abst. Kunst. 1912, **2**, 319.

[2] D. R. P. 193112, 207354. U. S. P. 970029. E. P. 18341, 1907. F. P. 380358, 1907; abst. C. A. 1908, **2**, 1642; 1909, **3**, 2070; J. S. C. I. 1908, **27**, 32, 514; 1910, **29**, 1173; Chem. Zentr. 1908, I, 784; 1909, I, 1296; Chem. Ztg. Rep. 1908, **32**, 42; 1909, **33**, 182; Wag. Jahr. 1908, II, 326; 1909, II. 228; Zts. ang. Chem. 1908, **21**, 1094; 1909, **22**, 599.

[3] It would appear that in addition to the above described "vegetable" amyloid, there exists a protein amyloid which gives a characteristic carbohydrate reaction with iodine, notwithstanding its animal origin, differing from all other known products of degeneration in not being formed in the organism in any phase of the normal or physiological life, and therefore must be looked upon as a pathological product. Amyloid—like hyalin—is regarded as a modification coagulation product of the circulating proteid, probably serum albumen, not fibrin. Detailed information concerning this body is to be found in the writings of F. Herz (Chem. Ztg. **16**, 1594; abst. J. C. S. 1893, **64**, i, 447); N. Krawkow (Centr. Med. Wiss. 1892, 145; Bied. Centr. **21**, 753; J. C. S. 1893, **64**, i, 288; Arch. exp. Path. Pharm. 1897, **40**, 195; J. C. S. 1898, **74**, ii, 42); C. Neuberg (Verh. Deut. Path. Ges. 1904, p. 19; Chem. Centr. 1904, II, 1576); C. Hanson (Biochem. Zts. 1908, **13**, 185; J. C. S. 1908, **94**, ii, 968); M. Mayeda (Zts. physiol. Chem. 1909, **58**, 469; J. C. S. 1909, **96**, i, 274); L. Crie (Compt. rend. 1879, **88**, 759; J. C. S. 1879, **36**, 613); S. Kostiurina (Chem. Centr. 1887, 120; J. C. S. 1887, **52**, 506); A. Tschermak (Zts. physiol. Chem. 1895, **20**, 343; J. C. S. 1895, **68**, i, 255).

For amylocellulose, see E. Fernbach (Compt. rend. 1904, **138**, 819; abst. J. C. S. 1904, 819; J. S. C. I. 1904, **23**, 449); E. Roux (Compt. rend. 1905, **140**, 440; J. S. C. I. 1905, **24**, 285); J. Wolff (Woch. f. Brau. 1906, **23**, 31; J. S. C. I. 1906, **25**, 139; Woch. f. Brau. 1906, **23**, 216; J. S. C. I. 1906, **25**, 716).

For amylase, refer to P. Petit (Compt. rend. 1904, **138**, 1231; J. S. C. I.

stituent of the cell wall,[1] and (like starch) yields a blue coloration with iodine, whence its name. R. Reiss[2] found on digestion with sulfuric acid it yielded dextrose. It was as far back as 1846 that J. Poumarede and L. Figuier[3] described their "*modification sulfurique*" and called commercially "Papyrine," obtained from ordinary filter paper by treatment with sulfuric acid, and later called vegetable parchment. E. Blondel,[4] and C. Guignet[5] and others investigated the formation of amyloid from cellulose by hydrolysis or hydration, but with conflicting conclusions.

Blondel observed that when sulfuric acid was brought together with cotton, those places where the acid came in direct contact with the fabric gave much deeper dyeings, especially with xylidine ponceau.

Guignet in saturating dry cotton cellulose with 50° Bé. sulfuric acid noted that the jelly-like mass which is formed without rise in temperature is stable in the presence of an excess of the acid, but on heating quickly passes into dextrin. After treatment with water and washing until neutral, the "colloidal cellulose" is said to be substantially soluble in water, and can be nitrated without change in form.

M. Mendelsohn and E. Frankel[6] manufacture amyloid by treating substances rich in cellulose, especially wood meal, with a mixture of sulfuric acid and sodium sulfate, or with sodium acid

---

1904, **23**, 616); J. Effront (Mon. Sci. 1904, **18**, 561; J. S. C. I. 1904, **23**, 831); L. Brasse, Bied. Centr. **14**, 169; J. S. C. I. 1885, **4**, 460); J. Effront (Compt. rend. 1905, **141**, 626; J. S. C. I. 1905, **24**, 1183; Mon. Sci. 1895, **45**, 541, 711; J. S. C. I. 1896, **15**, 127).

[1] Ber. 1892, **25**, 1237; Zts. physiol. Chem. 1892, **17**, 353; abst. J. C. S. 1892, **62**, i, 803; 1893, **64**, i, 127; J. S. C. I. 1892, **11**, 763; Bull. Soc. Chim. 1892, **8**, 971; 1893, **10**, 414; Chem. Centr. 1892, I, 820; Jahr. Chem. 1892, 2149; Chem. Ztg. Rep. 1892, **16**, 144.

[2] Ber. 1889, **22**, 609; Landw. Jahr. 1889, **18**, 761; abst. J. C. S. 1889, **56**, 687; J. S. C. I. 1889, **8**, 406; Bull. Soc. Chim. 1890, **3**, 713; Chem. Centr. 1889, I, 541; Jahr. Chem. 1889, 2086.

[3] Compt. rend. 1846, **23**, 918; 1847, **25**, 17; J. prakt. Chem. 1847, **42**, 25; Ann. 1847, **64**, 387; Rev. Sci. 1847, **14**, 68; Soc. Philom. Proc. Verb. 1846, 130; J. Pharm. 1847, (3), **11**, 81; Rep. Pharm. (2), **47**, 344; abst. Annuaire de Chim. 1847, 453; Jahr. Chem. 1847–1848, **1**, 797.

[4] Bull. soc. ind. Rouen, 1882, **10**, 471.

[5] Compt. rend. 1889, **108**, 1258; abst. J. S. C. I. 1889, **8**, 1001; J. C. S. 1889, **56**, 847; Chem. Centr. 1889, II, 124; Jahr. Chem. 1889, 2839; Chem. Ztg. Rep. 1889, **13**, 194; Chem. Tech. Rep. 1889, I, 145; Wag. Jahr. 1889, **35**, 1180; Ber. 1889, **22**, R, 574; Mon. Sci. 1889, **33**, 986; Chem. News, 1889, **60**, 24.

[6] D. R. P. 220634, 1908; abst. C. A. 1910, **4**, 2202; J. S. C. I. 1910, **29**, 777; Chem. Zentr. 1910, I, 1476; Chem. Ztg. Rep. 1910, **34**, 200; Zts. ang. Chem. 1910, **23**, 958.

sulfate, the amyloid being subsequently precipitated with water and separated from the liquid. By proceeding in this manner the patentees claim little or no dextrin is formed, the resulting amyloid when fermented and saccharified yielding a spirit nearly free from fusel oil.

In the process for producing colloidal cellulose as disclosed by L. Lilienfeld,[1] 100–200 parts of cellulose in small amounts is added to 1000 parts of sulfuric acid of 60° Bé. at 1°–8°, and after the cellulose has become nearly transparent and homogeneous, it is precipitated by the addition of water, washed until neutral, and then dissolved in 5% aqueous NaOH to a 5% solution of cellulose. By making faintly acid with HCl or acetic acid, a fine flocculent precipitate results, which, when washed with water and dried at a low temperature gives a colloidal cellulose especially desirable for subsequent nitration or alkylation, or for the formation of artificial filaments, either by the cuprammonium, zinc chloride or viscose processes.

In general,[2] when the action of sulfuric acid has been allowed to proceed at relatively low temperatures and for a short period, the products possess little or no reducing properties, but on the other hand if the sulfuric acid has remained in contact with the cellulose for a long time, or the solution has been allowed to rise in temperature during the treatment, then the resulting product acquires strong reducing properties. Long continued action of concentrated sulfuric acid imparts to the product strong reducing properties, grape sugar being finally obtained.

E. Flechsig[3] has shown that when certain conditions are maintained, the reaction may be made quantitative, the total amount of cellulose present being converted into grape sugar.

Hydrocellulose.[4] The compound or compounds resulting

[1] Aust. P. 63524, 1914.

[2] For other data on amyloid, consult A. Trecul, Compt. rend. 1858, **47**, 687. Schulze, Zts. physiol. Chem. 1894, **19**, 38. Votocek, Zts. Zuckerind. 1902–1903, **27**, 708. E. Bourquelot and H. Herissey, Compt. rend. 1900, **130**, 42, 731; 1901, **133**, 302. H. Herissey, Compt. rend. 1900, **130**, 1719. E. Hansen, Mitteil. Carlsberg Labor. 1879, **2**. Beijerinck, Centr. Bakteriol. 1898, **2**, (2), 213. A. Meyer, Ber. botan. Ges. 1901, 428.

[3] Zts. physiol. Chem. 1883, **7**, 523; Zts. deutsche Spiritusfabr. 1883, 805; abst. Ber. 1883, **16**, 2508; Chem. Tech. Rep. 1883, II, 144; Jahr. Chem. 1883, 1363; Wag. Jahr. 1883, **29**, 681; Tech. Chem. Jahr. 1883–1884, **6**, 275.

[4] J. Briggs, Papierfabrikant, 1910, **8**, 46; Chem. Ztg. 1910, **34**, 455; abst. J. S. C. I. 1910, **29**, 622; Jahr. Chem. 1910, II, 422; Bull. Soc. Chim. 1911, **10**, 60; C. A. 1910, **4**, 2372. E. Berl and R. Klaye, Zts. Schiess. Spreng.

from the hydrolysis of normal or unmodified cellulose by means of dilute acids has been termed "hydrocellulose," and appears to be a combination of cellulose with one molecule of water and therefore has been given the empirical formula $C_{12}H_{22}O_{11}$. This

---

1907, **2**, 381; abst. C. A. 1908, **2**, 184; J. C. S. 1908, **94**, i, 504; J. S. C. I. 1907, **26**, 1157; Chem. Zentr. 1908, I, 1381; Chem. Ztg. Rep. 1908, **32**, 43; Jahr. Chem. 1905–1908, II, 976. G. Büttner and J. Neumann, Zts. ang. Chem. 1908, **21**, 2609; 1909, **22**, 585; abst. Chem. Zentr. 1909, I, 441, 1471; C. A. 1909, **3**, 1168, 1457; J. C. S. 1909, **96**, i, 86, 290; Bull. Soc. Chim. 1909, **6**, 879; J. S. C. I. 1909, **28**, 105. C. Cross, Ber. 1911, **44**, 153; abst. Kunst. 1912, **2**, 14; Chem. Zentr. 1911, I, 519; J. S. C. I. 1911, **30**, 204; J. C. S. 1911, **100**, i, 114; C. A. 1911, **5**, 1513; Bull. Soc. Chim. 1911, **10**, 1297; Rep. chim. Pure, 1911, **11**, 232. C. Cross and E. Bevan, Chem. Ztg. 1909, **33**, 368; abst. C. A. 1909, **3**, 1589; J. C. S. 1909, **96**, i, 290; Chem. Zentr. 1909, I, 1471; Bull. Soc. Chim. 1909, **6**, 985; Chem. Tech. Rep. 1909, **33**, 216. H. Ditz, J. prakt. Chem. 1908, (2), **78**, 343; Chem. Ztg. 1907, **31**, 833, 844, 857; abst. C. A. 1907, **1**, 2941; J. C. S. 1907, **92**, i, 129; Bull. Soc. Chim. 1907 (4), **2**, 1468; Chem. Zentr. 1907, II, 1606; Jahr. Chem. 1905–1908, II, 964; Meyer Jahr. Chem. 1907, **17**, 504; Wag. Jahr. 1907, II, 507; Zts. ang. Chem. 1908, **21**, 1185. C. Cross, E. Bevan and C. Smith, J. C. S. 1897, **71**, 1001; Proc. Chem. Soc. 1897, 150; abst. Meyer Jahr. Chem. 1897, **7**, 154; J. S. C. I. 1897, **16**, 691; Chem. Centr. 1897, II, 544, 614; Jahr. Chem. 1897, 1502. C. Guignet, Compt. rend. 1889, **108**, 1258; abst. J. C. S. 1889, **56**, 847; Amer. J. Pharm. 1889, **61**, 568; Mon. Sci. 1889, **33**, 987; J. S. C. I. 1889, **8**, 1001; Chem. Tech. Rep. 1889, I, 145, 194; Ber. 1889, **22**, 574; Wag. Jahr. 1889, **35**, 1180; Chem. News, 1889, **60**, 24; Jahr. Chem. 1889, 2839. H. Jentgen, Zts. ang. Chem. 1910, **23**, 1541; 1911, **24**, 11, 585; abst. C. A. 1911, **5**, 1187, 1677, 3153; Bull. Soc. Chim. 1911, **10**, 85; Chem. Zentr. 1911, I, 640, 1816; J. C. S. 1911, **108**, i, 115, 355; J. S. C. I. 1911, **30**, 125. T. Koerner, Zts. ang. Chem. 1908, **21**, 2353; Papier Ztg. 1908, **33**, 3702; abst. C. A. 1909, **3**, 484. L. Mangin, Compt. rend. 1890, **110**, 295, 644; abst. Ber. 1892, **25**, R-109; Jahr. Chem. 1890, 2184; J. C. S. 1890, **58**, 734. O. Miller, Ber. 1910, **43**, 3430; 1911, **44**, 728; abst. J. C. S. 1911, **100**, i, 17, 355; Kunst. 1912, **2**, 14; C. A. 1911, **5**, 1187, 2175; Chem. Zentr. 1911, I, 355, 1164; Bull. Soc. Chim. 1911, **10**, 1150, 1297; Rep. Chim. 1911, **11**, 178, 323. W. Minajew, Zts. Farb. Ind. 1910, **9**, 65; abst. Chem. Zentr. 1910, I, 1304; Textil Färb. Ztg. **8**, 132; abst. C. A. 1910, **4**, 3006; Chem. Tech. Rep. 1910, **34**, 267. H. Ost and F. Westhoff, Chem. Ztg. 1909, **33**, 197; abst. C. A. 1909, **3**, 1394; J. S. C. I. 1909, **28**, 325; J. C. S. 1909, **96**, i, 210; Bull. Soc. Chim. 1909, **6**, 685; Jahr. Chem. 1909, II, 385. R. Scholl, Ber. 1911, **44**, 1312; abst. Kunst. 1911, 453; C. A. 1911, **5**, 3061; J. C. S. 1911, **100**, i, 525; Chem. Tech. Rep. 1911, **35**, 340. C. Schwalbe, Zts. ang. Chem. 1910, **23**, 1541; 1911, **24**, 12, 585; abst. Kunst. 1911, **1**, 452; J. S. C. I. 1911, **30**, 125; C. A. 1911, **5**, 1677; Chem. Zentr. 1911, I, 640; J. C. S. 1911, **100**, 115. A. L. Stern, Proc. Chem. Soc. 1894, 186; J. C. S. 1895, **67**, 74; abst. Chem. News, 1894, **70**, 267; Ber. 1895, **28**, R, 462; Jahr. Chem. 1894, 1132; Meyer Jahr. Chem. 1895, **5**, 524; Rev. gén. sci. 1895, **6**, 48. R. Oertel, Chem. Ztg. 1911, **35**, 713; abst. Chem. Zentr. 1911, II, 855; J. C. S. 1911, **100**, i, 607; J. S. C. I. 1911, **30**, 887. By the electrolysis of cellulose in a neutral potassium chloride bath the author has succeeded in transforming it into a product which is soluble in 10% sodium hydroxide and is probably a new hydroxycellulose. It can be obtained either as retaining the fibrous structure of cellulose or in such a form that it gives a milky, colloidal solution with water. L. Vignon. Compt. rend. 1900, **131**, 530, 708; abst. C. N. 1900, **82**, 255; J. C. S. 1901, **80**, i, 16; Chem. Ztg. 1900, II, 1151; J. S. C. I. 1900, **19**, 1102; Mon. Sci. 1900, **55**, 836; Rev. gén. sci. 1900, **11**, 1152; Rev. sci. 1900, **37**, II, 466;

is not to be confused with hydra-cellulose, which contains only water of hydration nor with the cellulose hydrates, the name applied by C. Cross and E. Bevan[1] to those modifications of cellulose containing in addition to hygroscopic moisture which is governed by atmospheric conditions, water of hydration which is dependent upon the constitutional structure and is more firmly held than ordinary hygroscopic moisture. With hydrocellulose, water apparently enters into chemical combination with the cellulose to form new derivatives. C. Schwalbe[2] has endeavored to differentiate between hygroscopic moisture and water of hydration by assuming that the former is entirely expelled at 100° while the latter is only driven off at the temperature of boiling toluene. But such a distinction has, in general, been found to be invalid.[3] The formation of hydrocellulose from cotton results in structural disintegration to such an extent that the fiber may readily be reduced to a fine powder. On account of the fact that it is much more reactive than ordinary cellulose, hydrocellulose is of considerable importance and has been employed for the production of the nitric and acetic esters of cellulose, as the hydrocellulose compounds, although less stable, are in general, more soluble in the solvents employed. In the art of cellulose acetylation therefore, hydrocellulose was formerly of considerable importance in that on account of its greater chemical reactivity cellulose was usually transformed first into hydrocellulose as a

Jahr. Chem. 1900, 840; Chem. Centr. 1900, II, 1069, 1151; 1901, I, 440; Bull. Soc. Chim. 1901, (3), **25,** 137. P. von Weimarn, Zts. Chem. Ind. Kolloide, 1912, **11,** 41; abst. Rev. Chim. Ind. 1913, **24,** 261; Zts. ang. Chem. 1913, **26,** R, 290; C. A. 1912, **6,** 3516; J. C. S. 1912, **102,** i, 679; J. S. C. I. 1912, **31,** 768; Chem. Zentr. 1912, II, 817; Chem. Ztg. Rep. 1913, **37,** 14. E. Jandrier, Compt. rend. 1899, **128,** 1407; abst. C. N. 1899, **80,** 11; J. C. S. 1899, **76,** i, 788; J. S. C. I. 1899, **18,** 711; Bull. Soc. Chim. 1899, **21,** 895; Chem. Centr. 1899, II, 184; Jahr. Chem. 1899, 1295. C. Bay, Zur Kenntnis der Hydro-, Oxy-, Hydral-, und Acid cellulosen. Giessen, 1913, 87.

[1] Proc. Chem. Soc. 1904, **20,** 90; abst. J. S. C. I. 1904, **23,** 557; Chem. News, 1904, **89,** 235; Rev. gén. sci. 1904, **15,** 522; Rep. gén. chim. 1904, **4,** 293; Chem. Centr. 1904, I, 1557; J. C. S. 1904, **85,** 691; Bull. Soc. Chim. 1904, **32,** 1301; Jahr. Chem. 1904, 1161.

[2] Ber. 1907, **40,** 1347, 4523; abst. J. S. C. I. 1907, **26,** 548, 1291; Chem. Zentr. 1907, I, 1490; 1908, I, 239; C. A. 1907, **1,** 1696, 2179; 1908, **2,** 1043; J. C. S. 1907, **92,** i, 390; 1908, **94,** i, 9; Zts. ang. Chem. 1907, **20,** 2166.

[3] Chem. Ztg. 1909, **33,** 197; abst. J. S. C. I. 1909, **28,** 325; J. C. S. 1909, **96,** i, 210; Chem. Zentr. 1909, I, 1231; C. A. 1909, **3,** 1394; Zts. ang. Chem. 1909, **22,** 1856; Rep. gén. chim. 1909, **9,** 321; Bull. Soc. Chim. 1909, **6,** 685. Zts. ang. Chem. 1908, **21,** 1321; abst. J. C. S. 1908, **94,** ii, 627; C. A. 1908, **2,** 2448; Bull. Soc. Chim. 1909, **6,** 58; Jahr. Chem. 1905–1908, II, 960; Chem. Zentr. 1908, I, 239.

separate method and the hydrocellulose thus formed subsequently acetylated. At the present time it is a question of considerable legal importance in patent litigation in the acetylation of cellulose in the presence of small amounts of catalyzers as sulfuric acid, as to whether the entire reaction is one of hydrocellulose formation and subsequent acetylation or whether acetylation is succeeded by partial hydrolysis, *i. e.*, whether the final product should be considered as acetylated hydrocellulose, or, more properly, hydrolyzed acetylcellulose. From a legal point of view the question has as yet never been adjudicated.

In the preparation of hydrocellulose according to the method of A. Girard,[1] cotton cellulose is placed at ordinary temperatures in sulfuric acid of sp. gr. 1.453 (55.5% H_2SO_4) when it is with a little swelling converted into friable cellulose after 10 to 12 hours immersion. When washed under proper precautions it retains its original fibrous state but is very friable and easily reduced to a powder.

According to B. Tollens[2] and G. Buettner and J. Neumann,[3]

[1] Compt. rend. 1875, **81**, 1105; abst. Ber. 1876, **9**, I, 65; Jahr. Chem. 1875, 786; Chem. Centr. 1876, 83; J. C. S. 1876, **30**, i, 696; Chem. News, 1875, **33**, 10; Amer. J. Sci. 1876, (3), **11**, 483; Schweizerische Wochenschrift f. Farmacie, June 2, 180; Pharm. J. and Trans. 1876–1877, (3), **7**, 26; Year Book of Pharm. 1877; Zts. des Oesterr. Apoth. Ver. 1876, 557; Chem. Tech. Rep. 1874, **14**, II, 179; Industrieblätter, 1876, 164; Dingl. Poly. 1876, **219**, 549. Ann. Chim. Phys. 1876, (5), **9**, 116; abst. Chem. Centr. 1877, 6. Compt. rend. **89**, 170; abst. Jahr. Chem. 1879, 1116; Chem. Centr. 1879, 582; Chem. Tech. Rep. 1879, **18**, II, 180; J. C. S. 1879, **36**, 911; Bull. Soc. d'Encour. (3), **8**, No. 91; Chem. News, 1881, **44**, 216; Bull. de la Soc. Franc. de Phot. 1879, **25**, 318; Mondes, **49**, 614; Publ. Ind. 1880, **26**, 46; J. A. C. S. 1879, 400; N. C. Eng. Mech. 1880, **30**, 420. Compt. rend. 1879, **88**, 1322; abst. Ber. 1879, **12**, II, 2085, 2158; Jahr. Chem. 1879, 835; J. de Pharm. 1879, **30**, 348; J. C. S. 1879, **36**, 779; Year Book Pharm. 1880, 80; Chem. Centr. 1879, 531; Mon. Sci. 1879, 958; Zts. f. d. Gesammte Brauwesen, 1879, 413; Wag. Jahr. 1879, **25**, 419, 1099. See also Wag. Jahr. 1876, 1066; Ann. Chim. Phys. 1881, (5), **24**, 337; abst. Ber. 1881, **14**, II, 2834; Jahr. Chem. 1881, 985; J. C. S. 1882, **42**, 378; Proc. U. S. Nav. Inst. 1882, **8**, 309; Bull. d'enc. **81**, 176; abst. Bull. Musee. **82**, 80; Naturforscher, **15**, 26. For the life of A. Girard, see M. L. Lindet, Bull. Soc. Chim. 1898, (3), 20; I–XXIV, with bibliography.

[2] J. Murumow, J. Sack and B. Tollens, Ber. 1901, **34**, 1431; abst. J. C. S. 1901, **80**, i, 453; J. S. C. I. 1901, **20**, 739; Bull. Soc. Chim. 1902, **28**, 269; Chem. Centr. 1901, II, 38; Jahr. Chem. 1901, 896. See also G. Bumcke and R. Wolffenstein, Ber. 1899, **32**, 2493; abst. J. C. S. 1899, **76**, i, 852; J. S. C. I. 1899, **18**, 940; Bull. Soc. Chim. 1900, **24**, 620; Chem. Centr. 1899, II, 752; Jahr. Chem. 1899, 1290; Meyer Jahr. Chem. 1899, **9**, 300. B. Tollens, Ber. 1901, **34**, 1434; abst. J. C. S. 1901, **80**, i, 1453; J. S. C. I. 1901, **20**, 269; Chem. Centr. 1901, II, 39; Jahr. Chem. 1901, 897.

[3] Zts. ang. Chem. 1908, **21**, 2609; abst. C. A. 1909, **3**, 1168; J. C. S. 1909, **96**, i, 86; J. S. C. I. 1909, **28**, 105; Chem. Zentr. 1909, I, 441; Chem. Ztg. Rep. 1909, **33**, 91; Jahr. Chem. 1905–1908, II, 960; Meyer Jahr. Chem.

maximum friability is attained with an acid of sp. gr. 1.52 to 1.54 but if the cotton is left in contact with the acid for too long a period the product is jelly-like and can then be washed only with great difficulty. Tollens[1] has prepared hydrocellulose by immersing 50 gm. of cotton in 280 gm. of sulfuric acid of sp. gr. 1.52 to 1.54 and after 12 to 14 hours immersion is first washed with water to neutrality, finally with alcohol and ether and dried in the air. However, G. Buettner and J. Neumann claim that when cellulose is treated with dilute sulfuric acid of sp. gr. 1.453 to 1.53 a mixture is formed consisting probably of hydrocellulose and oxycellulose, together with unchanged material. Under special conditions (using acid of only 3% to 4% strength), however, cellulose hydrates result of the general formula $(C_6H_{10}O_5)_x.H_2O$. Hydrocellulose of this composition, whether x = 2, 3, or 6, is a white, sandy powder, extremely resistant towards acids and alkalis. It is invariably not changed by boiling with dilute sulfuric acid, but is dissolved by cold concentrated sulfuric or fuming nitric acid and is only colored yellow on boiling with caustic potash or soda. Like cellulose, it is soluble in an ammoniacal solution of copper oxide. When the hydrocellulose, as prepared by the above investigators, is treated with acetic anhydride and concentrated sulfuric acid added, a vigorous reaction ensues, the substance dissolves, and on dilution with water an acetyl derivative is precipitated in white to blue opalescent flocks. This hydrocellulose is colored blue with zinc chloride-iodine reagent, or iodine and potassium iodide solution and is reduced by Fehling's solution or ammoniacal silver nitrate. They have been unable to corroborate Girard's statement that hydrocellulose is readily oxidized even at 50°, for the pure substance in their hands remained unchanged at 100°. If, however, traces of sulfuric acid are present decomposition ensues upon warming.[2]

Hydrocellulose may also be manufactured commercially by

1908, **18**, 195; Wag. Jahr. 1908, II, 492; Zts. ang. Chem. 1909, **22**, 585; abst. C. A. 1909, **3**, 1457; J. C. S. 1909, **96**, i, 290; Bull. Soc. Chim. 1909, **6**, 879; Chem. Zentr. 1909, I, 147; Jahr. Chem. 1909, II, 386; Wag. Jahr. 1909, II, 514.

[1] Ber. 1901, **34**, 1433; abst. J. C. S. 1901, **80**, i, 453.

[2] In another method recommended by A. Girard and extensively used, cotton cellulose is first saturated with sulfuric acid, pressed or centrifuged until it retains not more than 35% to 40% of its weight of liquid, allowed to dry in the air and then heated preferably in a sealed vessel for 8 to 10 hours at 35° to 40°, or 3 hours to 70°, and finally washed with water

the two methods of R. Stahmer. In the first one[1] chlorine is introduced into glacial acetic acid until the latter becomes distinctly yellow, when it is then heated to 60°-70°. The wood cellulose is then introduced with stirring, the cellulose swelling gradually so that it becomes necessary to use four to five times the amount of acetic acid to the cellulose. This voluminous mass after a short time again becomes thin, whereupon the resulting thin paste is washed to neutrality and dried. The temperature must not exceed 70°. It has been questioned as to whether or not oxycellulose rather than hydrocellulose is obtained by this method. It at least appears probable that mixtures of hydrocellulose and oxycellulose result. The latter also possesses, to a larger degree, the property of friability.

Instead of glacial acetic acid, R. Stahmer[2] recommends hydrochloric acid and potassium chlorate, 100 kilos of wood cellulose being introduced into a steam-jacketed kettle containing agitators, with 800 to 1000 kilos of crude hydrochloric acid of 21° Bé. (33.6% HCl), and when the mass reaches a temperature of 70°, approximately one kilo of potassium chlorate is added in small portions during the course of one to one and a half hours. After the mass has attained a pasty consistency, it is centrifugalized, washed and

---

and with ether. According to H. Mork and W. Walker (J. Frank. Inst. 1907, **164**, 136; abst. Mon. Sci. 1908, **60**, 461; C. A. 1908, **3**, 318), this method is uncertain in its results and does not yield uniform products. G. Buettner and J. Neumann also were unable to obtain a product of the same elementary composition as described by Girard when using his different methods of preparation.

[1] U. S. P. 679204, 1901; abst. Mon. Sci. 1901, (4), **57**, 284. F. P. 304723, 1900; abst. J. S. C. I. 1901, **20**, 469; Chem. Ztg. 1901, **25**, 270; Mon. Sci. 1900, (4), **59**, 20. D. R. P. 123121, 1900; abst. J. S. C. I. 1901, **20**, 1133; Zts. ang. Chem. 1901, **14**, 905; Chem. Centr. 1901, II, 567; Jahr. Chem. 1901, 892; Mon. Sci. 1900, (4), **59**, 9; Wag. Jahr. 1901, II, 612. E. P. 19039, 1900; abst. J. S. C. I. 1901, **20**, 926. See also D. R. P. Anmel. H-53315; abst. Kunst. 1912, **2**, 260. For acetylation of hydrocellulose prepared as above, see U. S. P. 692775, 1902; abst. J. S. C. I. 1902, **21**, 356; Mon. Sci. 1900, (4), **58–59**, 161. L. Lederer, D. R. P. 118538, 1901; abst. Wag. Jahr. 1901, II, 611; Chem. Centr. 1901, I, 712; Chem. Ztg. 1901, **25**, 271; Zts. ang. Chem. 1901, **14**, 345.

[2] U. S. P. 679203, 1901; abst. Mon. Sci. 1901, (4), **57**, 284. F. P. 309759, 1901; abst. J. S. C. I. 1902, **21**, 65; Mon. Sci. 1902, (4), **58**, 170. D. R. P. 123122, 1900; abst. J. S. C. I. 1901, **20**, 1133; Mon. Sci. 1902, (4), **58**, 9; Jahr. Chem. 1903, 892, 1014; Zts. ang. Chem. 1901, **14**, 905; Chem. Centr. 1901, II, 568; Wag. Jahr. 1901, II, 612. D. R. P. 137206, 1901; abst. Zts. ang. Chem. 1902, **15**, 1301; Chem. Centr. 1903, I, 107; Jahr. Chem. 1903, 1014; Wag. Jahr. 1902, **48**, I, 595. Aust. P. 8171, 1902. For acetylation of hydrocellulose prepared as above, see U. S. P. 692497, 1902; abst. J. S. C. I. 1902, **21**, 362; Mon. Sci. 1902, (4), **58**, 161. F. P. 308506, 1901; abst. J. S. C. I. 1902, **21**, 64; Mon. Sci. 1902, (4), **58**, 159.

dried. This product is said to possess in a high degree, resistance towards inorganic acids and the alkalis. The amount of potassium chlorate used is intended to be insufficient for the formation of oxycellulose, this latter reducing Fehling's solution, whereas the described product does not do so.

A. Stern[1] has shown that in the formation of hydrat-cellulose, under certain conditions there is invariably a loss in weight and not gain, as would be indicated by theory, from which he infers that a hydrat-cellulose is not always formed, but that a hydrocellulose occurs similar to that formed by other carbohydrates under comparable conditions.

A low degree of hygroscopicity is quite characteristic for the washed and dried hydrocelluloses which form white powders, and although their formation entails a great loss in tensile strength there at first is no change in form, for under the microscope the hydrocelluloses when reduced to a powder, still exhibit the structure of the cotton filament.

According to A. Girard,[2] hydrocelluloses are very sensitive to increased temperatures and begin to distinctly blacken at 100°. This statement of Girard is apparently due to the fact that he washed his preparations insufficiently, so that traces of the acid probably still remained. According to Ost,[3] very pure hydrocellulose is quite stable at 100° and in some instances up to as

---

[1] Proc. Chem. Soc. 1894, 186; J. C. S. 1895, **67**, 74; abst. J. S. C. I. 1894, **13**, 1230; Bull. Soc. Chim. 1896, (3), **16**, 1081; Ber. 1895, **28**, R, 462; Jahr. Chem. 1895, **48**, 1358; Meyer Jahr. Chem. 1895, **5**, 145, 524; Chem. News, 1894, **70**, 267; Chem. Centr. 1895, **66**, I, 29; Jahr. Chem. 1894, **47**, 1132. Proc. Chem. Soc. 1904, **20**, 43; J. C. S. 1904, **85**, 336; abst. Chem. News, 1904, **89**, 117; J. S. C. I. 1904, **23**, 265; Bull. Soc. Chim. 1904, **32**, 1175; Chem. Centr. 1904, **75**, I, 934, 1405; Chem. Ztg. 1904, **28**, 246; Jahr. Chem. 1904, **57**, 1161. In this connection see Proc. Chem. Soc. 1904, **20**, 90; J. C. S. 1904, **85**, 691; abst. Chem. News, 1904, **89**, 235; J. S. C. I. 1904, **23**, 557; Bull. Soc. Chim. 1904, **32**, 1301; Rep. Chim. 1904, **4**, 293; Chem. Centr. 1904, **75**, I, 1557; Jahr. Chem. 1904, **57**, 1161. See also M. Hoenig and S. Schubert, Monatsh. 1885, **6**, 708; 1886, **7**, 455; abst. Wein. Akad. Ber. **92** (2 Abth.), 737; Bull. Soc. Chim. 1886, (2), **46**, 517; Ber. 1885, **18**, 614; Jahr. Chem. 1885, **38**, 1576. Braconnot, Ann. Chim. Phys. 1819, (2), **12**, 185. Blondeau de Carolles, Ann. 1844, **52**, 412; J. prakt. Chem. 1844, **33**, 439. Fehling, Ann. 1845, **53**, 135; Marchand, J. prakt. Chem. 1845, **35**, 200. Bechamp, Ann. 1856, **100**, 364. Allihn, J. prakt. Chem. 1880, **130**, 61.

[2] Compt. rend. 1877, **88**, 1322; abst. J. C. S. 1879, **36**, 779; Bull. Soc. Chim. 1880, **34**, 507; Jahr. Chem. 1879, 835, 1116.

[3] Zts. ang. Chem. 1906, **19**, 994; abst. J. C. S. 1909, **90**, i, 560; Chem. Centr. 1906, II, 672; J. S. C. I. 1906, **25**, 606; Bull. Soc. Chim. 1906, **36**, 1058; Jahr. Chem. 1905–1908, II, 983; Meyer Jahr. Chem. 1906, **16**, 219; Wag. Jahr. 1906, **52**, II, 484.

high as 125°. This observation is corroborated by Witz,[1] while Stern found that when the hydrocelluloses are absolutely free from acid they do not turn black when heated up to 125°.[2] Hydrocellulose is sharply differentiated from normal cellulose by being colored blue with a solution of zinc chlor-iodide or with a solution of iodine in potassium iodide, and by reducing Fehling's solution and a solution of ammoniacal silver nitrate. Another important characterization of the hydrocelluloses are their power of dissolving in sodium hydroxide solutions with a marked reducing power. They resemble celluloses in exhibiting a great affinity for water, giving well defined hydrates of hydrocellulose, the extent of the hydrocellulose hydration being determined by the degree of hydrolysis; that is, the amount of water with which a cellulose will combine is dependent primarily upon the number of hydroxyl groups contained therein. Hydrocelluloses are but little changed by cold diluted acids, more so upon heating, when a yellow discoloration first appears, followed by decomposition. Schwalbe has determined that by boiling with 10% sodium hydroxide solution about 15% passes into solution. However, in 1% hot potassium hydroxide solution Girard's hydrocellulose apparently is unaffected, which is not in accordance with the experience of E. von Lippman.[3] Maximum solution, according to A. Girard, occurs at 160°,[4] and the undissolved residue has a decreased reducing power.[5] With all the hydrocelluloses, prolonged boiling will eventually lead to complete solution of the substances or else to a disappearance of the reducing property of the residue. W. Vieweg[6] has boiled hydrocellulose prepared with hydrochloric

---

[1] Bull. Rouen, 1882, **11**, 419; 1883, 169; abst. Jahr. Chem. 1883, 1782.

[2] J. C. S. 1904, **85**, 336; abst. Jahr. Chem. 1904, 1161; Proc. Chem. Soc. 1904, 43; Chem. Centr. 1904, I, 934, 1405; J. S. C. I. 1904, **23**, 265; Rev. gén. sci. 1904, **15**, 323; Bull. Soc. Chim. 1904, **32**, 1175.

[3] "Chemie der Zuckerarten," 1904, 3 Ed., 1519.

[4] Ann. Chim. Phys. 1881, (5), **24**, 366.

[5] C. Schwalbe, Zts. ang. Chem. 1907, **20**, 2170; Chem. Ztg. 1907, **31**, 937; abst. C. A. 1908, **2**, 704; Ber. 1907, **40**, 1961, 4523; J. C. S. 1908, **94**, i, 9; Jahr. Chem. 1905–1908, II, 961; Bull. Soc. Chim. 1908, **4**, 381; Chem. Zentr. 1908, I, 240.

[6] Papier Ztg. 1907, **32**, 130, 174; 1909, **34**, 149; Ber. 1907, **40**, 3880; 1908, **41**, 3269; abst. C. A. 1907, **1**, 1320; 1908, **2**, 3403; J. C. S. 1907, **92**, i, 893; 1908, **94**, i, 857; J. S. C. I. 1907, **26**, 836, 1157; 1908, **27**, 1081; Bull. Soc. Chim. 1908, (4), **4**, 902; Rep. Chim. 1908, **8**, 62; Chem. Zentr. 1907, II, 1780; 1908, II, 1584; Chem. Ztg. Rep. 1908, **32**, 27, 619; Meyer Jahr. Chem. 1907, **17**, 215; 1908, **18**, 506; Zts. ang. Chem. 1908, **21**, 1184.

acid for 15 to 20 minutes with normal sodium hydroxide solution and then titrated back with semi-normal sulfuric acid, and has found that upon prolonged boiling the hydrocellulose takes unto itself alkali hydroxides. In this way he determines the "acid number," which indicates the amount of alkali taken up. C. Schwalbe, on the other hand,[1] has demonstrated that cellulose also absorbs or consumes alkali upon analogous treatment. This determination, therefore, so far as the differentiation of the hydrocellulose given is inaccurate because the amount of alkali consumed apparently bears no definite ratio to the form of cellulose or hydrocellulose operated upon.

More recently W. Vieweg,[2] has stated that the acid number is in no measure influenced by hydrocellulose, which statement is diametrically opposite to the results of his earlier researches.

According to C. Cross and E. Bevan,[3] the residues described by A. Stern,[4] and having the empirical composition of cellulose, are no doubt products of hydrolysis and reversion, and are constitutionally different from the original cellulose, but are in no case identical with those described by Girard and therefore this investigator's exhaustive account of the action of acids on cellulose is not in accordance with analytical determinations observed by C. Cross and E. Bevan. They call attention to the fact that inasmuch as cellulose is of a chemically labile and structurally plastic character, occupying a position intermediate between the

---

1. Papier Ztg. 1909, **35**, 691, 994. Compare A. Luck and A. Durnford, E. P. 4769, 1895; abst. J. S. C. I. 1896, **15**, 134; Chem. Ztg. 1896, **20**, 652; Chem. Tech. Rep. 1896, **35**, 498, who describe a process for producing nitrocellulose in a dense powdery form, the essence of their invention being to destroy the structure of the cotton by treatment with H_2SO_4 and water, or aqueous zinc chloride, with subsequent nitration.

2. Papier Ztg. 1909, **35**, 890; compare 1910, **35**, 994; Wochenblatt f. Papier Fabr. 1910, **40**, 1255.

3. Proc. Chem. Soc. 1904, **20**, 90; J. C. S. 1904, **85**, 691; abst. Chem. News, 1904, **89**, 235; J. S. C. I. 1904, **23**, 557; Bull. Soc. Chim. 1904, **32**, 1301; Rep. Chim. 1904, **4**, 293; Chem. Centr. 1904, **75**, I, 1557; Jahr. Chem. 1904, 1161. Chem. Ztg. 1909, **33**, 368; abst. C. A. 1909, **3**, 1589; J. C. S. 1909, **96**, i, 290; Bull. Soc. Chim. 1909, (4), **6**, 985; Chem. Zentr. 1909, **80**, I, 1471. C. Cross, E. Bevan and C. Smith, J. C. S. 1897, **71**, 1005; Chem. News, 1896, **74**, 177; 1897, **76**, 188; abst. J. S. C. I. 1897, **16**, 691; Bull. Soc. Chim. 1898, **20**, 62; Chem. Centr. 1897, **68**, II, 544, 614, 1028; Jahr. Chem. 1897, 1502; Meyer Jahr. Chem. 1897, **7**, 154.

4. In this connection see Proc. Chem. Soc. 1904, **20**, 43; J. C. S. 1904, **85**, 336; abst. Chem. News, 1904, **89**, 117; J. S. C. I. 1904, **23**, 265; Bull. Soc. Chim. 1904, **32**, 1175; Chem. Centr. 1904, **75**, I, 934, 1405; Chem. Ztg. 1904, **28**, 246; Jahr. Chem. 1904, 1161.

two extreme products formed from ordinary cellulose by the action of, first, alkali hydroxide, and second, the halogen hydracids, both in presence of water, the suggestion is made that the terms hydra-cellulose and hydrocellulose, respectively, should properly be retained to designate two groups of derivatives obtained by processes "a" and "b" above mentioned. Hydrocellulose upon being brought in contact with concentrated potassium hydroxide swells up and gives a blue coloration with iodine, which it did not do previous to alkaline treatment, or at least to any great extent.

According to B. Tollens,[1] those hydrocelluloses prepared with sulfuric acid are not colored by concentrated sodium hydroxide, while those prepared with this acid of high concentration form colloids which partially dissolve with yellow discoloration. From these solutions, however, flocculent precipitates result by the addition of hydrochloric acid, and upon heating with concentrated potassium hydroxide, there is obtained acetic acid, oxalic acid and acetone, whereas upon boiling with lime, iso-saccharic acid was found by Tollens among the products of decomposition. Hydrocellulose upon heating with alkalis under pressure, forms acetic acid; and with saturated potassium carbonate solution, as high as 14% of acetic acid has been found where the temperature has been raised from 100° to 110°.[2]

On heating with alkali for eight hours in a closed vessel, 41.7% of acetic acid has been formed and this yield, it has been stated, may be materially increased by the addition of oxidizing agents. With cold diluted inorganic acids hydrocelluloses are unusually stable, less so with hot acids. Tollens has recorded that he was able to effect only slight solution and formation of but little glucose on boiling for eight hours with sulfuric acid of 3%.[3] Cotton cellulose is less resistant than is hydrocellulose, the residue of such boiling possesses, according to G. Buettner and J. Neumann,[4] giving the same elementary composition as the

---

1. Ber. 1901, **34**, 1432; abst. J. C. S. 1901, **80**, i, 453; J. S. C. I. 1901, **20**, 739; Chem. Centr. 1901, **72**, II, 39; Bull. Soc. Chim. 1902, **28**, 269; Jahr. Chem. 1901, 897.
2. C. Cross, E. Bevan and J. Isaac, J. S. C. I. 1892, **11**, 966; abst. Chem. Ztg. 1893, **16**, 1863; Chem. Centr. 1893, **64**, I, 407; Ber. 1893, **26**, R, 594; Mon. Sci. 1893, **41**, 889.
3. Tollens, Ber. 1901, **34**, 1433.
4. Zts. ang. Chem. 1908, **21**, 2609.

original material. On boiling with acids a small amount of furfural has been detected.[1] When pressure is used this resistance to decomposition is materially reduced. As is well known, hydrocellulose is more readily saccharified under pressure than is cotton cellulose. This statement is corroborated from the experiments of T. Koerner,[2] who, upon heating 40 grams of hydrocellulose prepared with 4% of sulfuric acid and fermentation, found that the fermented filtrate contained 18 grams of alcohol for each 100 grams of hydrocellulose. These results lack importance in that no comparative value for cotton cellulose was determined at the same time under comparable conditions. Girard found that when hydrocellulose is heated to 180° for eight to ten hours with 5% sulfuric acid, much carbon dioxide is evolved and elemental carbon separated.

According to B. Tollens,[3] zinc chloride-iodide solutions react bluish violet with hydrocellulose prepared with sulfuric acid, but the general observation has been that nearly all the hydrocelluloses react likewise. The color is quite fugitive against water which is a point in contradistinction to those of the hydrat-celluloses. Hydrocellulose reacts with fuchsine in sulfur dioxide not at all or only faintly,[4] but due to the fact that filter paper always contains small but variable amounts of oxycellulose, the content of the latter is responsible for the fact that filter paper usually reacts with sulfur-dioxide-fuchsine. L. Vignon has stated

---

1. L. Vignon, Compt. rend. 1898, **126**, 1355; abst. J. C. S. 1898, **74**, i, 620; J. S. C. I. 1898, **17**, 680; Bull. Soc. Chim. 1898, **19**, 810; Mon. Sci. 1898, **51**, 454; Rev. gén. sci. 1898, **9**, 918; Chem. Centr. 1898, **69**, II, 24, 972; Chem. Ztg. 1898, **22**, 425; Jahr. Chem. 1898, 2265. Cross and Bevan, Researches, I, 70.

2. Dissertation, Dresden, 1907, 35; compare Zts. ang. Chem. 1908, **21**, 2357; abst. J. S. C. I. 1908, **27**, 1216; J. C. S. 1908, **94**, 955; Chem. Zentr. 1908, **79**, II, 2049; Papier Ztg. 1908, **33**, 3702; C. A. 1909, **3**, 484. See also E. Simonsen, Zts. ang. Chem. 1898, **11**, 195, 219, 962, 1007; abst. Chem. Centr. 1898, **69**, I, 808; II, 144, 1148; J. S. C. I. 1898, **17**, 365, 481, 1164; J. C. S. 1899, **76**, i, 471; Bied. Centr. 1899, **28**, 200; Festschrift tech. Schule, Christiania, 1898, 22; Norsk. teknisk. Tidskr. 1895, 65; abst. Bied. Centr. 1896, **25**, 47; J. C. S. 1896, **70**, 331. Papier Ztg. 1903, **28**, 1787; Zts. ang. Chem. 1903, **16**, 572; abst. J. S. C. I. 1903, **22**, 814. See also W. Gentzen and L. Roth, D. R. P. 147844; abst. Chem. Centr. 1904, **75**, I, 410; Chem. Ztg. 1904, **28**, 66; Wag. Jahr. 1904, **49**, II, 370; Zts. ang. Chem. 1904, **17**, 244. A. Classen, D. R. P. 118540; abst. Chem. Ztg. 1901, **25**, 252; Wag. Jahr. 1901, **47**, II, 280; Zts. ang. Chem. 1901, **14**, 348.

3. Ber. 1901, **34**, 1432; abst. J. C. S. 1901, **80**, i, 453; J. S. C. I. 1901, **20**, 740; Bull. Soc. Chim. 1902, **28**, 269; Chem. Centr. 1901, **72**, II, 39; Jahr. Chem. 1901, 897.

4. C. Schwalbe, Zts. ang. Chem. 1907, **20**, 2171.

that hydrocellulose does not possess reducing properties,[1] whereas Cross and Bevan have shown that in alkaline solutions reduction takes place. According to B. Tollens,[2] hydrocellulose prepared by the process of Girard is also inert toward Fehling's solution, but H. Ost. has demonstrated[3] that slight reduction of cellulose prepared with sulfuric acid of 3% results, whereas C. Schwalbe[4] has proven beyond question that hydrocellulose possesses characteristic reducing properties in contradistinction to the hydratcellulose and pure normal or cotton cellulose. For a series of hydrocelluloses the following values have been found:

	Copper Number	Hygroscopic Water
Hydrocellulose cotton with concentrated H_2SO_4, precipitated by H_2O	7.9	5.3
Hydrocellulose: cotton with H_2SO_4 of 45° Bé	3.9	6.3
Hydrocellulose: cotton with HCl gas	4.0	3.8
Hydrocellulose: cotton with H_2SO_4 of 3%	5.6	3.6
Hydrocellulose: absorbent cotton with H_2SO_4 of 3%	5.2	...
Hydrocellulose: filter paper with H_2SO_4 of 3%	6.2	3.8
Hydrocellulose from parchment with H_2SO_4 of 3%	8.7	6.0
Hydrocellulose: mercerized cotton with H_2SO_4 of 3%	8.8	6.3

The hydrocelluloses, however, prepared by the process of Stahmer with hydrochloric acid and potassium chlorate, are said not to possess reducing properties and not to reduce either ammoniacal silver nitrate or Fehling's solution. The hydrocelluloses dissolve much more readily than ordinary cotton in cuprammonium solution. E. Bronnert,[5] on the other hand, in his patent application, states that solution takes place at the best but slowly

[1] Compt. rend. 1898, **126**, 1355; abst. J. C. S. 1898, **74**, 620; Jahr. Chem. 1898, 2265; J. S. C. I. 1898, **17**, 680; Chem. Centr. 1898, **69**, II, 24; Bull. Soc. Chim. 1898, **19**, 810; Mon. Sci. 1898, **51**, 454.

[2] Ber. 1901, **34**, 1432; abst. J. C. S. 1901, **80**, i, 453; J. S . C. I. 1901, **20**, 739; Chem. Centr. 1901, II, 38.

[3] Zts. ang. Chem. 1906, **19**, 994; abst. J. S. C. I. 1906, **25**, 606; Bull. Soc. Chim. 1906, **36**, 1058; J. C. S. 1906, **90**, i, 560; Chem. Centr. 1906, II, 672.

[4] Zts. ang. Chem. 1907, **20**, 2170; Chem. Ztg. 1907, **31**, 937; abst. C. A. 1908, **2**, 704; Ber. 1907, **40**, 4523; J. C. S. 1908, **94**, i, 9.

[5] D. R. P. 109996. See also Aus. P. 3638. Fr. P. 278371. U. S. P. 646381. E. P. 13331, 1899; abst. Mon. Sci. 1901, (4), **57**, 20; Wag. Jahr. 1900, II, 448; Jahr. Chem. 1900, 843; Chem. Centr. 1900, **71**, I, 231; Chem. Ztg. 1900, **24**, 426.

and imperfectly. C. Schwalbe, in a sample prepared by means of 3% sulfuric acid,[1] found ready solubility. Hydrocellulose is not difficultly soluble in zinc chloride-hydrochloric acid mixtures, whereas with zinc chloride solution alone without the addition of hydrochloric acid, hydrocellulose is readily soluble, especially in syrupy phosphoric acid. The affinity of hydrocellulose toward dyestuffs has been but imperfectly and inconclusively studied. Statements available are in large part contradictory, presumably because hydrocellulose of very different modes of preparation have been used for the experiments, and also from the fact that undoubtedly in many instances traces of acids were not entirely eliminated from the hydrocellulose after formation.

G. Witz claims hydrocellulose does not dye with such basic dyes as methyl violet or methylene blue,[2] whereas Ost found that hydrocellulose gives a light shade with fuchine, deeper however, than cotton cellulose.

Hydrocellulose is often confounded with hydrat-cellulose; statements applying to the latter, therefore, are confusing. Schwalbe has observed that one and the same hydrocellulose dyes strongly with methylene blue and less powerfully with diamond green than cotton cellulose.[3] Statements in general show that a thorough investigation of the numerous types of dyestuffs as to their behavior against hydrocellulose is necessary before tangible data can be established as to their deportment in this respect. Against oxidizing agents, however, especially of the oxygen of the air, hydrocellulose is sensitive. Solutions of permanganate are reduced,[4] this oxidation leading to the formation of oxalic and saccharic acids. For the detection of hydrocellulose, the diminished tensile strength, potassium iodide-iodine test, the hygroscopicity and especially the reducing properties may be utilized.

H. Ditz[5] considers it possible to distinguish the hydrocelluloses from oxycellulose by means of Nessler's reagent. The same

1. C. Schwalbe, Zts. ang. Chem. 1907, **20**, 2171.
2. Bull. soc. chim. Rouen, 1883, **11**, 220.
3. "Faerbetheorien," page 85.
4. L. Kollmann, Zentr. f. d. Oester. Papier. Ind. 1909, 408; 1910, 709; Papierfabr. 1910, **8**, 863, 890; abst. J. S. C. I. 1910, **29**, 1151; Chem. Ztg. Rep. 1910, **34**, 455.
5. J. prakt. Chem. 1908, **78**, 343; abst. J. S. C. I. 1908, **27**, 1129; J. C. S. 1908, **94**, i, 954; Chem. Zentr. 1908, II, 2000; C. A. 1909, **3**, 841; Bull. Soc. Chim. 1909, **6**, 1176; Chem. Ztg. Rep. 1908, **32**, 619.

applies as to reducing property, by a quantitative determination of the reducing power when the presence of either hydrocellulose or oxycellulose can be detected.

According to G. Buettner and J. Neumann, however,[1] it is impossible to produce by the same method of preparation, bodies of the same elementary composition, and therefore it is impossible, contrary to the contention of these authors, to determine accurately by ultimate analysis the hydrocellulose content of a cellulose derivative, quite apart from the fact that the ultimate analysis does not permit of the differentiation between hydrocellulose and hydrat-cellulose derivatives. However, we know with certainty that hydrocellulose contains more water than cotton cellulose. A. Girard's investigations conform to the formula $(C_6H_{10}O_5)_2.H_2O$. A. Stern, on the other hand,[2] alleges to have obtained figures conforming more nearly to the formula $C_6H_{10}O_5$, but it must be remembered that he boils the initial material with acid of 5%. H. Ost was unable to obtain such high figures,[3] his results leading to the formula $(C_6H_{10}O_5)_6.H_2O$. T. Koerner[4] and G. Buettner and J. Neumann[5] have obtained still different results. It is only upon boiling the hydrocellulose prepared by Buettner and Neuman with dilute sulfuric acid (one to one) that figures are found by analysis conforming to $(C_6H_{10}O_5)_6.H_2O$. As all these hydrocelluloses were prepared from filter paper, it is natural to assume that they represent in reality a mixture of hydrocellulose containing smaller amounts of oxycellulose. The general proposition, however, has been repeatedly, experimentally and analytically demonstrated that the hydrocelluloses also contain more water than normal cellulose, but the amount

---

[1] Zts. ang. Chem. 1908, **21**, 2609; Wochenblatt. 1909, **40**, 17; abst. C. A. 1909, **3**, 1168; J. S. C. 1909, **96**, i, 86; J. S. C. I. 1909, **28**, 105; Chem. Zentr. 1909, I, 441; Chem. Ztg. Rep. 1909, **33**, 91; Jahr. Chem. 1905–1908, II, 960; Meyer Jahr. Chem. 1908, **18**, 195; Wag. Jahr. 1908, II, 492.

[2] J. C. S. 1904, **85**, 336; abst. Chem. News, 1904, **89**, 117; J. S. C. I. 1904, **23**, 265; Bull. Soc. Chim. 1904, **32**, 1175; Chem. Centr. 1904, I, 934, 1405; Chem. Ztg. 1904, **28**, 246; Jahr. Chem. 1904, 1161.

[3] Zts. ang. Chem. 1906, **19**, 994; abst. J. C. S. 1906, **90**, i, 560; J. S. C. I. 1906, **25**, 606; Bull. Soc. Chim. 1906, **36**, 1053; Chem. Centr. 1906, **77**, II, 672; Jahr. Chem. 1905–1908, II, 983; Meyer Jahr. Chem. 1906, **16**, 219; Wag. Jahr. 1906, **52**, II, 484.

[4] Dissertation, Dresden, 1907, 34; compare Zts. ang. Chem. 1908, **21**, 2357; abst. J. S. C. I. 1908, **27**, 1216; J. C. S. 1908, **94**, 955; Chem. Zentr. 1908, **79**, II, 2049; Papier Ztg. 1908, **33**, 3702; C. A. 1909, **3**, 484.

[5] Zts. ang. Chem. 1908, **21**, 2609; 1909, **22**, 585.

of this water depends in a large measure upon the method of operation and these methods have not as yet been worked out satisfactorily.

Cotton cellulose also is capable of permanently fixing a small amount of metal as copper from dilute solutions of cupric salts, while the corresponding acids remain almost quantitative in the solution. Unbleached cotton takes up relatively much, bleached cotton less of these metals. The small amount of metal which is nevertheless absorbed after the purification is due, according to B. Rassow[1] to the presence of oxycellulose. Cellulose hydrate and hydrocellulose do not take up any copper from solutions of its salts, the "copper sulfate equivalent" should therefore be a valuable adjunct to Schwalbe's "copper equivalent" in the characterization and differentiation of celluloses. Nickel sulfate, aluminum sulfate and potassium chloride behave towards bleached cotton like copper salts. Artificial silks which contain oxycellulose fix these metals better than ordinary cotton. This fixation apparently is independent of the concentration of the solutions, temperature and the time. Silver nitrate is reduced by the various celluloses. R. Haller[2] has shown that the presence of nitrogenous matter in the lumen of the cotton fiber accounts for the fiber being readily dyed by saffranine. The hydrocelluloses esterify, and especially acetylate, much more readily than normal cotton cellulose. At 180°, as first shown by Schützenberger, hydrocellulose reacts almost quantitatively with acetic anhydride but with profound decomposition, the pulverulent hydrocellulose being converted into a viscid syrup which is precipitable by water. Hydrocellulose prepared according to the methods of Stahmer with glacial acetic acid and chlorine are alleged to give acetyl derivatives of special chemical and physical properties in that they dissolve in nitric acid to a clear reddish brown liquid from which a nitro-compound may be thrown out by water. Hydrocelluloses prepared with hydrochloric acid and

---

1. Zts. ang. Chem. 1911, **24**, 1127; abst. J. Soc. Dyers Col. 1911, **27**, 214; Chem. Ztg. 1911, **35**, 645; abst. C. A. 1912, **6**, 684; J. S. C. I. 1911, **30**, 1307; Chem. Ztg. Rep. 1911, **35**, 340; Meyer Jahr. Chem. 1911, **21**, 514; Wag. Jahr. 1911, **57**, II, 503.

2. J. Soc. Dyers Col. 1907, **23**, 167; Zts. Farbenind. 1907, **6**, 125; abst. J. S. C. I. 1907, **26**, 523; Chem. Zentr. 1907, **78**, II, 953; Chem. Ztg. Rep. 1907, **31**, 257; Jahr. Chem. 1905–1908, II, 3185; Zts. ang. Chem. 1907, **20**, 2085.

potassium chlorate under the same conditions, however, are said to be more difficultly susceptible to acetylation.

W. de Coninck has shown[1] that after filter paper has stood in ordinary hydrochloric acid for 18 hours at 28°, the liquid does not reduce Fehling's solution, whereas after 62 hours contact, the solution on boiling turns brown and a brownish black precipitate, partly soluble in ammonia, is formed (humus). On the other hand, cotton, while it does no reduce Fehling's solution, does not turn brown on boiling. In fuming hydrobromic acid it dissolves in a few minutes with amber color, changing to black the following day. A small amount of humus in this instance is formed, and the liquid appreciably reduces Fehling's solution.

J. Ville and W. Mestrezat[2] have found that dilute hydrofluoric acid (5% to 30%) has little effect on cellulose, while the more concentrated acid brings about destructive hydrolysis. By heating on the water bath with 50% acid for six hours, a 50% yield of dextrose is obtained.

According to the observations of R. Scholl[3] the reducing properties of modified cellulose in its action toward Fehling's solution may be shown by its behavior with certain "vat dyestuffs." Flavanthrene, a yellow dyestuff which gives a blue "vat" on reduction, is said to be particularly suitable for these experiments. Reduced "flavanthrene vat" prepared by boiling 0.03 gram of flavanthrene with a little dilute sodium hydroxide and solid sodium hydrosulfite, when used to treat cellulose for a few seconds develops a dark blue liquid.

C. Schwalbe,[4] who has hydrated cotton cellulose by the action of concentrated alkalis and acids, finds there is no difference between the product of the reaction and cellulose itself insofar as their reducing action on Fehling's solution is concerned. Dilute acids hydrolyze cellulose to hydrocellulose which has a

[1] Bull. Sci. acad. Roy. Belg. 1910, 587; abst. J. C. S. 1910, **98**, i, 654; C. A. 1911, **5**, 1585.

[2] Compt. rend. 1910, **150**, 783; abst. J. C. S. 1910, **98**, i, 301; C. A. 1910, **4**, 2094; J. S. C. I. 1910, **29**, 483; Rev. gén. sci. 1910, **21**, 311; Bull. Soc. Chim. 1910, **7**, 372; Chem. Zentr. 1910, I, 1781.

[3] Ber. 1911, **44**, 1312; abst. J. S. C. I. 1911, **30**, 739; J. C. S. 1911, **100**, i, 525; Chem. Zentr. 1911, II, 80; C. A. 1911, **5**, 3061; Bull. Soc. Chim. 1911, **10**, 1644; Rep. gén. chim. 1911, **11**, 408.

[4] Chem. Ztg. 1907, **31**, 937; abst. J. S. C. I. 1907, **26**, 1107; C. A. 1908, **2**, 704; Zts. ang. Chem. 1907, **20**, 2170; Ber. 1907, **40**, 4523; J. C. S. 1908, **94**, i, 9.

much higher reducing power than cellulose. Vegetable parchment and Chardonnet silk are both able to reduce Fehling's solution, though not so much as the hydrocellulose. According to Schwalbe, parchment owes its reducing power to the production of a small quantity of hydrocellulose formed while the concentrated acid is being washed out during the process of preparation. On the other hand, the reducing action of Chardonnet silk is due primarily to the production of oxycellulose by the nitric acid employed in its preparation. These oxycelluloses, moreover, are distinguished from the hydrocelluloses by being much more strongly colored by basic dyestuffs. Mercerized cotton, Pauly silk and viscose silk have scarcely any reducing action on Fehling's solution.

C. Schwalbe,[1] in criticising the work of G. Beuttner and J. Neumann,[2] contests their view that elementary analysis is the best measure for the degree of re-solution in the case of hydrocellulose and that even if elementary analysis were sufficiently accurate it would fail to make any distinction between hydrocelluloses and cellulose hydrates. He contends that the cupric reduction method, on the other hand, is characteristic for hydrocelluloses and is in actual use and practice for the determination of the degree of hydrolysis, whereas Buettner and Neumann state that hydrocelluloses are extremely resistant toward alkalis and acids. It has been pointed out that their results merely show the residual hydrocellulose to have the same elementary composition after boiling with acids as it had before, and do not take into consideration account of the quantity of substance dissolved in the form of sugar as the result of the acid treatment. Similarly, Schwalbe contests the statement as to the resistance of hydrocelluloses toward alkalis. It is well known that sodium hydroxide at the boiling point dissolves a large proportion of the hydrocellulose and that the cupric reducing power of the residue is thereby diminished. This author quotes the following results which he has obtained by boiling Girard's hydrocellulose with 15% sodium hydroxide solution:

---

1. Zts. ang. Chem. 1909, **22,** 155; abst. J. S. C. I. 1909, **28,** 216; C. A. 1909, **3,** 1013.
2. Zts. ang. Chem. 1908, **21,** 2609; abst. J. S. C. I. 1909, **28,** 105; J. C. S. 1909, **96,** i, 86; Chem. Zentr. 1909, I, 441; C. A. 1909, **3,** 1168.

Hydrocellulose	Quantity of NaOH Solution of 15% Strength	Time of Boiling	Undissolved Residue
Gm.	Gm.	Min.	Per cent.
10	200	10	48
10	200	20	42
10	200	30	40
10	200	40	37
10	400	60	33

The blue color produced by zinc chloride-iodine reagent on hydrocellulose is said to be very transient and is rapidly removed by water, whereas the same coloration with cellulose hydrate resists the action of water for a considerable period of time. Whereas H. Taufs[1] has shown that the action of water on cellulose at high temperatures causes the formation of hydrocellulose, C. Schwalbe and M. Robinoff[2] found that only a chemically treated cellulose, e. g., filter paper or a bleached cellulose, underwent marked hydrolysis. Pure cellulose hydrolyzed but slowly, even at 30 atmospheres pressure; above 150° however, the action is marked. Pure cellulose was obtained by boiling pure, unbleached Egyptian cotton with hard soap solution, washing and carefully bleaching. The "corrected copper number" of this cellulose was 0.04. Bleaching with hypochlorite solution and the subsequent acid treatment caused formation of oxycellulose as was indicated by the increased copper number. Using an acid concentration of 0.1% hydrochloric acid or acetic acid, the copper number was 0.15. In cold solution, cotton cellulose is hydrolyzed most efficiently

---

1. Dingl. Poly. 1889, **273**, 276; abst. C. A. 1911, **5**, 1838; Jahr. Chem. 1889, 2838.

2. Zts. ang. Chem. 1911, **24**, 256; abst. C. A. 1911, **5**, 1838. See also C. Schwalbe, Ber. 1907, **40**, 4523, 4547; abst. J. S. C. I. 1907, **26**, 1293; J. C. S. 1907, **92**, i, 390; Zts. ang. Chem. 1907, **20**, 1735; Chem. Zentr. 1907, I, 1490; 1908, I, 239, 1264; Jahr. Chem. 1905–1908, II, 961; Chem. Ztg. 1907, **31**, 937; Bull. Soc. Chim. 1908, (4), **4**, 381; Zts. ang. Chem. 1907, **20**, 2166; abst. J. S. C. I. 1908, **27**, 35; Chem. Zentr. 1908, I, 239. Zts. ang. Chem. 1908, **21**, 1321; abst. J. C. S. 1908, **94**, ii, 627; Chem. Zentr. 1908, II, 447; C. A. 1908, **2**, 2448. Zts. ang. Chem. 1909, **22**, 155; abst. C. A. 1909, **3**, 1013; Chem. Zentr. 1909, I, 737. Zts. ang. Chem. 1909, **22**, 929; abst. C. A. 1909, **3**, 1457, 1811; Chem. Zentr. 1909, I, 1988. Zts. ang. Chem. 1910, **23**, 2030; abst. C. A. 1911, **5**, 1187. Zts. ang. Chem. 1911, **24**, 12; abst. C. A. 1912, **6**, 545; J. C. S. 1911, **100**, i, 115. Zts. ang. Chem. 1911, **24**, 256; abst. J. S. C. I. 1911, **30**, 277. Zts. ang. Chem. 1911, **24**, 1260; abst. J. C. S. 1911, **100**, i, 712; Kunst. 1911, **1**, 452; C. A. 1912, **6**, 545; see also C. A. 1911, **5**, 1187, 1677, 3153; J. C. S. 1911, **100**, i, 180.

by 4% alkali solution, a maximum copper number of 0.257 being obtained at this concentration. They found that the solubility of the cotton cellulose decreased with increasing concentration of alkali up to 9% strength, when the solubility is unappreciable at ordinary temperatures. Solubility also increases with rise in temperature, and above 150° it is considerable. The following table is given as the copper numbers obtained after hydrolysis of pure cellulose at various temperatures. It will be noted that the 4% solution, in each case, is the most efficient.

Room Temp.	Water	Strength of Alkali Solution				
		1%	2%	3%	4%	5%
100° F.	0.042	0.150	0.166	0.195	0.257	0.135
135°	0.109	0.180	0.200	0.262	0.528	0.168
150°	0.153	0.142	0.170	0.395	0.890	0.285
179°	0.300	.....	0.110	0.128	0.445	0.050
213°	.....	.....	.....	.....	.....	0.000

Where 3% sulfuric acid was allowed to act upon cellulose, C. Schwalbe found the resulting hydrocellulose gave a copper number of 5.2 (when made from binding twine) or 5.6 (from filter paper). There is a sharp difference between alkali-prepared hydrat-cellulose, and acid prepared hydrocellulose. H. Jentgen[1] finds for the preparation of hydrocellulose that Girard's method is difficult of control, and prefers to distribute the acid through the cellulose by means of a solvent which does not dissociate the acid, heating the material in the presence of an excess of solvent. Suitable solvents are glacial acetic acid, ether, amyl acetate, ethyl acetate, ethyl acetoacetate, formic acid and glycerol. He contends that the degree of formation of the cellulose into hydrocellulose is best shown by Schwalbe's cupric reduction method,[2] and that the formation increases with the time and temperature of the treatment up to a certain point when sulfuric acid is used. The formation is said to be very rapid, but the hydrocellulose tends to gelatinize on washing. The copper value of hydrocellulose thereby falls generally between four and six, but higher and lower values are occasionally obtained. Several salts of

---

[1] Zts. ang. Chem. 1910, **23**, 1541; abst. J. S. C. I. 1910, **29**, 1052.

[2] Zts. ang. Chem. 1910, **23**, 924; abst. J. S. C. I. 1910, **29**, 689.

strong acids with weak bases also convert cellulose into hydrocellulose under similar conditions, the action of these salts being direct and not depending on dissociation as has often been assumed. In the production of hydrocellulose the acid is said to enter into association with the cellulose by adsorption, and hydrolysis proceeds by the action of finely divided water on the adsorption compound, the acid acting as a contact agent. It is therefore necessary that the acid be in a finely divided, concentrated (molecular or non-ionized) condition. Where moisture is rigorously excluded, which is very difficult to insure, the cellulose may be recovered practically unchanged by washing the adsorption compound with water. Hydrocellulose prepared as above is soluble in all the solvents of cellulose and is attacked by strong sulfuric acid in the same manner as cellulose. Strong caustic soda lye dissolves a portion of the hydrocellulose (generally about one-third), the residue being mercerized and the copper value thereby reduced. About 85% of the soluble portion is reprecipitated by acid; the remainder being permanently soluble and profoundly decomposed. In the case of hydrocellulose, the refraction colors of ordinary cotton cellulose in polarized light are considerably diminished.

In a subsequent communication[1] in defining his viewpoints as to the fact that acids such as sulfuric acid are only capable of hydrolyzing cellulose when they are finely distributed in a molecular condition, and that ionized acids have no such action, this author points out the following: 1st, that 1% concentrated solutions of acid have practically no hydrolyzing action on cellulose; 2nd, that alcoholic solutions of acids hydrolyze only very slowly and the rate of hydrolysis is directly influenced by the dissociated capacity of the solvent; 3rd, that 1% solution of acid in non-dissociating solvents hydrolyze cellulose rapidly. In the preparation of hydrocellulose by Girard's method, where the cellulose is steeped in a 3% solution of sulfuric acid, the former must be dried in the air before the acid will act, whereby the latter be-

---

[1] Zts. ang. Chem. 1910, **23**, 1541; abst. C. A. 1911, **5**, 1187. Zts. ang. Chem. 1911, **24**, 11; abst. J. C. S. 1911, **100**, i, 115; J. S. C. I. 1911, **30**, 125. See also Schwalbe, Zts. ang. Chem. 1911, **24**, 12, 1260; C. A. 1911, **5**, 1187. Zts. ang. Chem. 1911, **24**, 585; Kunst. 1911, **1**, 452; J. C. S. 1911, **100**, i, 355. See also C. Schwalbe, Zts. ang. Chem. 1911, **24**, 12; abst. J. C. S. 1911, **100**, i, 115.

comes concentrated to about 30%, at which concentration sufficient molecular sulfuric acid is adsorbed by the cellulose to effect its disintegration. In the production of hydrocellulose it is assumed that the adsorption compound is formed between molecular sulfuric acid and cellulose and that water must be present, but not in sufficient quantity to cause complete ionization of the acid, and that the adsorbed acid then promotes reaction between the cellulose and the water and acts as a catalyst. The production of such an adsorption compound is assumed in ester reaction, e. g., in acetylation as a primary phase, esterification being secondary and hydrolysis being tertiary. Similarly, nitric acid also forms adsorption compounds with cellulose as a primary stage and nitration is secondary. Schwalbe, replying to the above contentation, holds that dilute aqueous acids do have a distinct hydrolyzing action on cellulose, and that cellulose may be prepared by Girard's method by steeping cellulose in acid of only 0.001% concentration. If this cellulose be dried in the air the acid present will have a concentration of only 0.02% but will still hydrolyze the cellulose. The contentions of Jentgen have repeatedly been brought into question by Schwalbe.

The following[1] are intermediate products of the hydrolysis of cotton cellulose by means of sulfuric acid:

Guignet's cellulose[2] is prepared by triturating 5 gms. of air-dry cotton wool in a mortar with 85 cc. of 62.5% sulfuric acid for 15 minutes, digesting the mass at the ordinary temperature for 5 hours, diluting with 175 cc. of water, filtering off on a cloth and washing the precipitate by decantation until free from acid. It gives colloidal solutions which are stable on boiling and may be re-constituted after evaporation to dryness, but which are coagulated by small quantities of acids and salts, also on the addition of alcohol. It is distinguished by its low hydrolysis value (Schwalbe); it is only colored blue by iodine solution in presence

[1] C. Schwalbe and W. Schulz, Ber. 1910, **43**, 913; abst. J. C. S. 1910, **98**, i, 301. Zts. ang. Chem. 1913, **26**, 499; abst. J. S. C. I. 1913, **32**, 499; C. A. 1910, **4**, 1751; Jahr. Chem. 1910, **63**, II, 419.

[2] Compt. rend. 1889, **108**, 1258; abst. Ber. 1889, **22**, 574; Jahr. Chem. 1889, **42**, 2839; Chem. Centr. 1889, **60**, II, 124; J. C. S. 1889, **51**, 847; Chem. News, 1889, **60**, 24; J. S. C. I. 1889, **8**, 1001; Chem. Ztg. Rep. 1889, **13**, 194; Chem. Tech. Rep. 1889, I, 145; Wag. Jahr. 1889, **35**, 1180; Mon. Sci. 1889, **33**, 986.

of sulfuric acid, whereas vegetable parchment gives a blue coloration direct.

Flechsig's amyloid[1] is prepared by treating 5 gm. of cotton with a cooled mixture of 30 gm. of 92% sulfuric acid and 10 gm. of water. The acid is allowed to act for 1–2 hours at a temperature between 6° and 30°. The sticky mass is coagulated by dilution and washed free from acid. The washed product can be dried at 95° without decomposition but not at 105°. It is colored blue by iodine in presence of sulfuric acid. It possesses colloidal properties, but in a less pronounced degree than Guignet's cellulose; it has higher copper value, hydrolysis value and solubility in alkali than Guignet's cellulose.

Parchmentized cellulose is prepared by immersion for 10–30 seconds in 78% sulfuric acid. The properties vary according to whether loose cotton or filter paper is treated. Parchmentized cotton wool, when boiled with 10% sodium hydroxide for 15 minutes, is dissoved to the extent of 70%, but filter paper similarly treated loses only 18%. It absorbs cupric hydroxide from Fehling's solution and the last traces are removed only with difficulty by acid; the hydrolysis value is high, the copper value is relatively low. It is stained blue by iodine without the intervention of sulfuric acid.

Ekström's acid cellulose is prepared by treating 5 gm. of cotton in a mortar with 18 gm. of 78% sulfuric acid for 45 minutes, then diluting with 29 cc. of water and pressing the product between cloths. On stirring the residue with a little water a colloidal solution is obtained, but with much water the product is parchmentized. It is colored blue by iodine without sulfuric acid. It has high copper and hydrolysis values and is completely soluble in alkali.

J. Briggs[2] has found that cellulose is converted by oxalic acid, slowly at the ordinary temperature, more rapidly at higher temperatures, partly into a hydrocellulose and partly into a compound which is considered as an acid oxalate of hydrocellulose. The ester exhibits, even in the form of its sodium salt, a strong affinity

---

[1] Zts. physiol. Chem. 1883, **7**, 523; abst. Zts. deutsche Spiritusfabr. 1883, 805; Ber. 1883, **16**, 2508; Chem. Tech. Rep. 1883, **21**, II, 144; Jahr. Chem. 1883, **36**, 1363; Wag. Jahr. 1883, **29**, 681; Tech. Chem. Jahr. 1883–1884, **6**, 275.

[2] J. S. C. I. 1912, **31**, 520; abst. J. C. S. 1912, **102**, i, 539.

for basic dyestuffs, as well as for the substantive dyestuffs. Mork has described processes for the esterification of hydrocellulose[1] without change of form. Many methods have been devized for the commercial acetation of hydrocellulose, either with sulfuric[2]

---

[1] U. S. P. 854374, 1907; abst. J. S. C. I. 1907, **26**, 713; Mon. Sci. 1907, **66**, 159; C. A. 1907, **1**, 2316. For the preparation of "alkali-hydrocellulose," see Vereinigte Kunstseidefabriken, A. G. F. P. 323475, 1902; abst. J. S. C. I. 1903, **22**, 508. E. P. 17501, 1902; abst. J. S. C. I. 1903, **22**, 817.

[2] U. S. P. 692497, 1902; abst. J. S. C. I. 1902, **21**, 362; Mon. Sci. 1908, (4), **58**, 161. F. P. 308506, 1901; abst. J. S. C. I. 1902, **21**, 64; Mon. Sci. 1902, (4), **58**, 159. U. S. P. 654988, 1900; abst. Mon. Sci. 1901, (4), **57**, 98. E. P. 11749, 1900; abst. J. S. C. I. 1901, **28**, 741. D. R. P. 118538, 1899; abst. Mon. Sci. 1901, **57**, 213; Zts. ang. Chem. 1901, **14**, 345; Chem. Centr. 1901, **72**, I, 712; Jahr. Chem. 1901, **54**, 891; Chem. Ind. 1901, **24**, 330. D. R. P. 120713, 1900; being addn. to D. R. P. 118538; abst. Mon. Sci. 1901, **57**, 283; Chem. Ind. 1901, **24**, 453; Zts. ang. Chem. 1901, **14**, 575; Chem. Centr. 1901, **72**, I, 1219. F. P. 301749, 1900; abst. Mon. Sci. 1901, **57**, 63. U. S. P. 708456, 708457; abst. J. S. C. I. 1902, **21**, 1243; Mon. Sci. 1903, (4), **60**, 165. U. S. P. 999236, 1911; abst. J. S. C. I. 1911, **30**, 1050. E. P. 3103, 1907; abst. J. S. C. I. 1907, **26**, 889. F. P. 374370, 1907; abst. J. S. C. I. 1907, **26**, 776; Mon. Sci. 1908, **68**, 84; Chem. Zts. 1907, **6**, 139. F. P. 324718, 1903; abst. J. S. C. I. 1903, **22**, 620. E. P. 4886, 1902; abst. J. S. C. I. 1903, **22**, 315. F. P. 316500, 1901; abst. J. S. C. I. 1902, **21**, 719; Mon. Sci. 1903, **59**, 53. Aust. P. 17456, 1902. D. R. P. Anm. L-15737. E. P. 22237, 1911; abst. J. S. C. I. 1912, **31**, 279. F. P. 435507, 1911; abst. J. S. C. I. 1912, **31**, 329. Belg. 239564, 1911. U. S. P. 679204, 1901; abst. Mon. Sci. 1901, **57**, 284. F. P. 304723, 1900; abst. J. S. C. I. 1901, **20**, 469; Chem. Ztg. 1901, **25**, 270; Mon. Sci. 1900, (4), **59**, 20. D. R. P. 123121, 1900; abst. J. S. C. I. 1901, **20**, 1133; Zts. ang. Chem. 1901, **14**, 905; Chem. Centr. 1901, **72**, II, 567; Mon. Sci. 1900, **59**, 9; Jahr. Chem. 1901, **54**, 892. E. P. 19039, 1900; abst. J. S. C. I. 1901, **20**, 926. U. S. P. 854374, 1907; abst. J. S. C. I. 1907, **26**, 713; Mon. Sci. 1907, **67**, 159. U. S. P. 922340, 1909; abst. J. S. C. I. 1909, **28**, 671. F. P. 400652, 1909; abst. J. S. C. I. 1909, **28**, 1061; Mon. Sci. 1910, **73**, 165. D. R. P. 237718, 1907; abst. Zts. ang. Chem. 1911, **24**, 1988; Chem. Zentr. 1911, **82**, II, 922; Chem. Ind. 1911, **34**, 573; Chem. Ztg. Rep. 1911, **35**, 481. It. P. 303–136–101262, 1909. U. S. P. 734123, 1903; abst. J. S. C. I. 1903, **22**, 961; Mon. Sci. 1903, **60**, 173. U. S. P. 790565, 1905; abst. J. S. C. I. 1906, **24**, 686. D. R. P. 153350, 1901; abst. Zts. ang. Chem. 1904, **17**, 1697; Chem. Centr. 1904, **75**, II, 625; Jahr. Chem. 1904, **57**, 1168; J. C. S. 1904, **86**, i, 853; Chem. Ind. 1904, **27**, 538. D. R. P. 159524, 1901; abst. Chem. Centr. 1905, **76**, II, 527; Zts. ang. Chem. 1905, **18**, 1636; Jahr. Chem. 1905–1908, II, 984; J. C. S. 1906, **90**, i, 6; Chem. Ind. 1905, **28**, 535. F. P. 317007, 1901; abst. J. S. C. I. 1902, **21**, 870; Mon. Sci. 1903, **60**, 54. E. P. 21628, 1901; abst. J. S. C. I. 1902, **21**, 870. Aust. P. 31391. It. P. 62042, 1901. U. S. P. 953677, 1910; abst. J. S. C. I. 1910, **29**, 557. U. S. P. 955082, 1910; abst. J. S. C. I. 1910, **29**, 557; Mon. Sci. 1910, **73**, 131. E. P. 17036, 1909; abst. J. S. C. I. 1910, **29**, 1005. F. P. 405293, 1909; abst. J. S. C. I. 1910, **29**, 417; Mon. Sci. 1910, **73**, 171; Chem. Ztg. Rep. 1910, **34**, 75. D. R. P. 219162, 219163, 1907; abst. Jahr. Chem. 1910, **63**, I, 426; Zts. ang. Chem. 1910, **23**, 768; Chem. Ind. 1910, **33**, 186; Wag. Jahr. 1910, **56**, II, 433; Chem. Zts. 1910, **9**, 1986, 1988. Aust. P. 45765, 1909. Hung. Anm. N-952, July 21, 1909. Ital. P. 103978, 1909. Belg. P. 198984, 198985, 1907; 217837, 1909.

or phosphoric acids;[1] or iodine,[2] both at normal[3] and reduced pressures.[4] Hydrocellulose benzoates,[5] formates[6] and sulfonates[7] have also been described but they are not commercially manufactured at the present time. Water-soluble and alcohol-soluble cellulose acetates result from the acetation of hydrocelluloses prepared according to Stahmer;[8] for the manufacture of lakes[9] and the toughening of gas mantles with hydrocellulose acetates,[10] consult Volume VIII.

---

1. E. P. 4886, 1902; abst. J. S. C. I. 1903, **22**, 315. F. P. 316500, 1901; abst. J. S. C. I. 1902, **21**, 719; Mon. Sci. 1903, **59**, 53. Aust. P. 17456, 1902. D. R. P. Anm. L-15737.

2. U. S. P. 679204, 1901; abst. Mon. Sci. 1901, **57**, 284. F. P. 304723, 1900; abst. J. S. C. I. 1901, **20**, 469; Chem. Ztg. 1901, **25**, 270; Mon. Sci. 1900, **59**, 20. D. R. P. 123121, 1900; abst. J. S. C. I. 1901, **20**, 1133; Zts. ang. Chem. 1901, **14**, 905; Chem. Centr. 1901, **72**, II, 567; Mon. Sci. 1900, **59**, 9; Jahr. Chem. 1901, **54**, 892. E. P. 19039, 1900; abst. J. S. C. I. 1901, **20**, 926.

3. E. P. 2511, 1907; abst. J. S. C. I. 1907, **26**, 634; J. Soc. Dyers Col. 1907, **23**, 215. F. P. 376262, 1907; abst. J. S. C. I. 1907, **26**, 988; Mon. Sci. 1908, **68**, 87. D. R. P. 189836, 189837, 1908; abst. Zts. ang. Chem. 1908, **21**, 268; Jahr. Chem. 1905–1908, II, 983; J. C. S. 1908, **94**, i, 321; Chem. Ind. 1907, **30**, 617. U. S. P. 679203, 1901; abst. Mon. Sci. 1901, **57**, 284; F. P. 309759, 1901; abst. J. S. C. I. 1902, **21**, 65; Mon. Sci. 1902, **58**, 170. D. R. P. 123122, 1900; abst. J. S. C. I. 1901, **20**, 1133; Mon. Sci. 1902, **58**, 9; Jahr. Chem. 1903, 1014; Zts. ang. Chem. 1901, **14**, 905; Chem. Centr. 1901, **72**, II, 568.

4. U. S. P. 1030311, 1912; abst. J. S. C. I. 1912, **31**, 680; C. A. 1912, **6**, 2528; Chem. Ztg. 1912, **36**, 485. Can. P. 139046, 1912; abst. C. A. 1912, **6**, 1526. E. P. 25893, 1912; abst. J. S. C. I. 1912, **31**, 279.

5. E. P. 22237, 1911; abst. J. S. C. I. 1912, **31**, 279. F. P. 435507, 1911; abst. J. S. C. I. 1912, **31**, 329. Belg. P. 239564, 1911.

6. U. S. P. 953677, 1910; abst. J. S. C. I. 1910, **29**, 557. U. S. P. 955082, 1910; abst. J. S. C. I. 1910, **29**, 557; Mon. Sci. 1910, **73**, 131. E. P. 17036, 1909; abst. J. S. C. I. 1910, **29**, 1005. F. P. 405293, 1909; abst. J. S. C. I. 1910, **29**, 417; Mon. Sci. 1910, **73**, 171; Chem. Ztg. Rep. 1910, **34**, 75. D. R. P. 219162, 219163, 1907; abst. Jahr. Chem. 1910, I, 426; Zts. ang. Chem. 1910, **23**, 768; Chem. Ind. 1910, **33**, 186; Wag. Jahr. 1910, **56**, II, 433; Chem. Zts. 1910, **9**, 1986, 1988. Aust. P. 45765, 1909. Hung. Anm. N-952, July 21, 1909. Ital. P. 103978, 1909. Belg. P. 198984, 198985, 1907; 217837, 1909.

7. D. R. P. 200334, 1907; abst. J. S. C. I. 1908, **27**, 1130; Mon. Sci. 1911, **74**, 63; Chem. Zts. 1908, **7**, 909; Zts. ang. Chem. 1908, **21**, 2233; Chem. Zentr. 1908, **79**, 655; Jahr. Chem. 1905–1908, 987; J. C. S. 1908, **94**, i, 955; Chem. Ind. 1908, **31**, 499.

8. U. S. P. 679204, 1901; abst. Mon. Sci. 1901, **57**, 284. F. P. 304723, 1900; abst. J. S. C. I. 1901, **20**, 469; Chem. Ztg. 1901, **25**, 270; Mon. Sci. 1909, **59**, 20. D. R. P. 123121, 1900; abst. J. S. C. I. 1901, **20**, 1133; Zts. ang. Chem. 1901, **14**, 905; Chem. Centr. 1901, **72**, II, 567; Mon. Sci. 1900, **59**, 9; Jahr. Chem. 1901, 892. E. P. 19039, 1900; abst. J. S. C. I. 1901, **20**, 926.

9. U. S. P. 692497, 1902; abst. J. S. C. I. 1902, **21**, 362; Mon. Sci. 1902, **58**, 161. F. P. 308506, 1901; abst. J. S. C. I. 1902, **21**, 64; Mon. Sci. 1902, **58**, 159.

10. F. P. 324718, 1903; abst. J. S. C. I. 1903, **22**, 620.

The cellulose regenerated from any of these solutions differs from the untreated material in being more reactive and in containing a larger proportion of hydrogen and oxygen. The elementary composition agrees well with the formula $(C_{12}H_{10}O_{10}).H_2O$ or some mixture of this with normal cellulose. Treatment of cellulose with acids and alkalis yields eventually very similar products. Those obtained by the hydrolysis of nitrocellulose and other cellulose esters possess analogous characteristics. There are, however, considerable differences between celluloses which have been treated by the different processes. Those celluloses which have been mercerized and the alkali washed out or have been treated into viscose and cellulose regenerated therefrom, are not as reactive with Fehling's solution as cellulose that has undergone acid treatment. The hydrate celluloses in general give off the extra water at a temperature of 120° to 125°,[1] whereas hydrocellulose retains its water more obstinately and at this temperature eliminates less than the untreated celluloses.[2]

Action of Ozone on Cellulose. As previously stated, according to M. Cunningham and C. Doree,[3] ozone in concentration of 1% to 2% rapidly attacks cotton, forming a cellulose peroxide and an acid derivative together with some carbon dioxide, the peroxide being decomposed at 80°. The acid may be removed by boiling with water or digestion with decinormal alkali, the neutral residue then obtained being an oxycellulose. The acidity

---

1. H. Ost and F. Westhoff, Chem. Ztg. 1909, **33**, 197; abst. J. S. C. I. 1909, **28**, 325; Chem. Zentr. 1909, I, 1231. See also O. Hauser and H. Herzfeld, Chem. Ztg. 1915, **39**, 689; abst. C. A. 1915, **9**, 3128. Compare C. A. 1908, **2**, 184, 704, 1043, 1882; 1909, **3**, 1013, 1108, 1457, 1811; 1910, **4**, 1369; 1911, **5**, 1187, 1677, 3153; 1912, **6**, 545; 1913, **7**, 2303; 1914, **8**, 1009. See H. Ost, Zts. ang. Chem. 1906, **19**, 993; abst. Chem. Centr. 1906, II, 673; J. C. S. 1906, **90**, i, 560; J. S. C. I. 1906, **25**, 606; Bull. Soc. Chim. 1906, **36**, 1053; Jahr. Chem. 1905–1908, II, 983; Meyer Jahr. Chem. 1906, **16**, 219; Wag. Jahr. 1906, **52**, II, 484.

2. For other applications of hydrocellulose, see Heberlein & Co., F. P. 468821, 1914; abst. C. A. 1915, **9**, 2315. Hide-ite Leather Co. E. P. 14527, 1912. F. P. 445279; abst. Kunst. 1913, **3**, 176. J. Hinde, Can. P. 77779. H. MacFarland and R. Shoemaker, U. S. P. 1146189, 1915; abst. C. A. 1915, **9**, 2432. A. Nobel & Co., D. R. P. 4410, 1878; abst. Wag. Jahr. 1879, 419; Deut. Ind. Ztg. 1879, 171; Ber. 1879, **12**, 712; Chem. Ztg. 1879, **3**, 197; Dingl. Poly. 1879, **232**, 188; Chem. Ind. 1879, **2**, 171; Chem. Tech. Rep. 1879, I, 287; J. A. C. S. 1879, **1**, 303. J. Rice, D. R. P. 279167, 1913; abst. C. A. 1915, **9**, 1247; Wag. Jahr. 1914, **60**, II, 405; Chem. Ztg. Rep. 1914, **38**, 552; Zts. ang. Chem. 1914, **27**, 662; Chem. News, 1876, **33**, 10; 1899, **80**, 237; 1903, **87**, 20. Erfind. u. Erfahr. **7**, 625.

3. Proc. Chem. Soc. 1912, **28**, 38; abst. J. S. C. I. 1912, **31**, 278; J. C. S. 1912, **101**, 497; C. A. 1912, **6**, 1849; Chem. Zentr. 1912, **83**, I, 1818; Bull. Soc. Chim. 1912, **12**, 1129. Cf. Kolb, Bull. Soc. Ind. Mulhouse, 1868, 94.

and amount of carbon dioxide produced during treatment from one to twenty hours in duration, have been measured and the constants of the oxycellulose determined and compared with typical oxycelluloses. Lignocellulose jute is not appreciably affected unless moisture is present, in which case it is oxidized, giving carbon dioxide, acetic and formic acids and complex non-volatile acids which yield furfural. Quantitative treatment of this progressive action of the ozone has shown that the lignin group is rapidly attacked in the first three hours, after which the action becomes slower, the residue being then uniformly oxidized. The lignin reaction ceases when the loss in weight is about 33%. Direct evidence of ozonized formation has not been obtained, although the formation of formic and acetic acids appear to be due to decomposition of some product formed in the first instance by the action of ozone. In a continuation of their work on the same lignocellulose jute,[1] the action of ozone on the more complex tissues of wood has been examined. In the presence of moisture, ozone rapidly attacks the wood substance, producing CO_2 and acetic compounds. As a result of the oxidation, a considerable portion of the wood is converted into derivatives soluble in water, the loss after twelve hours being some 40% in weight. The water digest contains formic, acetic and other reducing acids and yields furfuraldehyde. The results are well explainable by the formulation of the lignin groups given by Cross and Bevan,[2] but do not lend weight to the coniferyl alcohol formula proposed by Klason. The action of ozone on purified cotton cellulose furnishes a peroxide recognized by its oxidizing action on potassium iodide solution.[3] In their investigation of this question it was found that with a high percentage of moisture a small amount of peroxide alone is produced, but in air-dried material the quantity of peroxide formed is very much greater and at the same time solid insoluble acid derivatives and oxycellulose result. The amount of "active oxygen" fixed by air-dried cotton, mercerized

---

[1] Proc. Chem. Soc. 1913, **29**, 104; abst. J. S. C. I. 1913, **32**, 482; J. C. S. 1913, **103**, 677; Chem. Zentr. 1913, **84**, II, 246; Bull. Soc. Chim. 1913, **14**, 950; Rev. gén. sci. 1913, **24**, 410; C. A. 1913, **7**, 2385.

[2] "Researches on Cellulose," III, 104.

[3] Proc. Chem. Soc. 1913, **29**, 222; abst. J. S. C. I. 1913, **32**, 695; C. A. 1913, **7**, 3661; J. C. S. 1913, **103**, 1347; Chem. Zentr. 1913, **84**, II, 1466; Bull. Soc. Chim. 1913, **14**, 1263.

cotton, and lustra-cellulose after 18 hours exposure to ozone, was 0.0056%, 0.0106% and 0.0248% respectively. The peroxide is slowly decomposed on treatment with water, hydrogen peroxide being generated. It is also decomposed to the extent of 25% after heating for two hours at 37° and almost entirely so after two hours at 95°. The activity appears to soon disappear if the material is kept in the air but persists for some weeks in a dry atmosphere. These properties recall the "photographic action" of the natural woods described by W. Russell[1] and has been shown to be due probably to the same cause, namely, the gradual production of hydrogen dioxide.

C. Doree[2] has investigated the effect of the treatment with ozone on the breaking strength and elongation of cotton, mercerized cotton and viscose silk, as shown in the following table.

The cotton yarns were successively extracted with alcohol, alcohol-ether, ether and water, then wetted out, pressed between the cloth, opened out and hung in a chamber through which ozonized oxygen (1.5% to 2% ozone) was continually passed. After exposure the yarns were immersed in water, pressed and dried:

The effect of 2% ozone on the chemical characters of cotton and viscose silk is shown in the following table, the copper num-

Time of Treatment	Relative Breaking Strength (B) and Elongation (E) after Treatment with Ozone for Different Periods. (Untreated Material = 100)									
	Egyptian Cotton				Grey Cotton 2/60		Grey Cotton 2–60 Mercerized		Viscose Silk, 120 Deniers	
	1/40		2/80							
Hrs.	B	E	B	E	B	E	B	E	B	E
0.5	100	99	103	92	99	96	..	..	106	99
1	99	84	100	84	94	103	97	104	98	90
3	91	80	88	76	82	97	92	100	86	70
6	88	78	70	65	65	82	82	94	73	54
12	53	52	44	47	52	70	70	76	53	21

---

[1] Phil. Trans. 1904, **197**, 281; Proc. Roy. Soc. 1904, **74**, 131; abst. J. S. C. I. 1904, **23**, 998; Jahr. Chem. 1904, **57**, 168; Rev. gén. sci. 1904, **15**, 917.

[2] J. Soc. Dyers Col. 1913, **29**, 205; abst. J. S. C. I. 1913, **32**, 746; C. A. 1913, **7**, 3029. See also J. S. C. I. 1912, **31**, 278; 1913, **32**, 482, 695.

	Cotton Wool		Mercerized Cotton Wool		Mercerized Yarn 2/60 Grey (Tension)		Viscose Silk 120 Deniers	
	Normal	After 24 hr. Ozone	Normal	After 24 hr. Ozone	Normal	After 24 hr. Ozone	Normal	After 24 hr. Ozone
Loss in weight, %.	....	12	....	7	....	...	....	4.5
C, per cent........	44.4	43.5	43.2	43.5	....	...	44.6	44.4
Methylene blue absorption.........	0.3	2.1	0.4	3.1	....	2:3	1.6	1.8
Copper number....	1.2	16.9	1.7	24.0	....	9.6	3.0	15.5
Loss in 10% KOH.	....	64	....	57	....	...	....	50

bers being determined by Schwalbe's method[1] and the methylene blue absorption by Vignon's method.[2] The loss of weight on both for ten minutes with 10% solution of potassium hydroxide was also determined:

Cellulose Peroxide. Cotton (as well as linen) fabrics which have been bleached and acidified without the subsequent use of an "antichlor," occasionally retain the property characteristic of "active oxygen," in that they liberate iodine from potassium iodide for a much longer time than is consistent with the emanating amounts of residual hypochlorites which may be present. C. Cross and E. Bevan[3] have recorded a case in which a cotton cloth, bleached, soured and washed under normal conditions,

---

[1] Ber. 1907, **40,** 1347; abst. J. S. C. I. 1907, **26,** 548; Zts. ang. Chem. 1910, **23,** 924; abst. J. S. C. I. 1910, **29,** 689. See also W. Vieweg, Papier Ztg. 1907, **32,** 130, 174; 1909, **34,** 149; Ber. 1907, **40,** 3880; 1908, **41,** 3269; abst. C. A. 1907, **1,** 1320; 1908, **2,** 3403; J. C. S. 1907, **92,** i, 893; 1908, **94,** i, 857; J. S. C. I. 1907, **26,** 836, 1157; 1908, **27,** 1081; Bull. Soc. Chim. 1908, (4), **4,** 902; Rep. Chim. 1908, **8,** 62; Chem. Zentr. 1907, **78,** II, 1780; 1908, **79,** II, 1584; Chem. Ztg. Rep. 1908, **32,** 27, 619; Meyer Jahr. Chem. 1907, **17,** 215; 1908, **18,** 506; Zts. ang. Chem. 1908, **21,** 1184.

[2] L. Vignon, Compt. rend. 1897, **125,** 448; Bull. Soc. Chim. 1898, **19,** 790; abst. J. S. C. I. 1897, **16,** 908; 1898, **17,** 917; J. C. S. 1898, **74,** i, 8; Rev. Phys. et Chim. 1897–1908, **2,** 21; Mon. Sci. 1897, **49,** 859; Chem. Zentr. 1897, **68,** II, 843; Chem. Ztg. 1897, **21,** 811; Jahr. Chem. 1897, **50,** 1506.

[3] Zts. ang. Chem. 1906, **19,** 2101; 1907, **20,** 570; abst. J. S. C. I. 1907, **26,** 44; 1908, **27,** 260; Papier Ztg. 1907, **32,** 87; Wochbl. Papierfabr. 1907, **38,** 384; abst. C. A. 1907, **1,** 1320, 2489; Chem. Zentr. 1907, **78,** I, 1537; 1908, **79,** II, 640; see also K. Rieth, Wochbl. Papierfabr. 1907, **38,** 394. According to D. Zimmermann (Zts. ang. Chem. 1907, **20,** 1280; abst. Chem. Zentr. 1907, **78,** I, 1537; II, 925) and E. Grandmougin (Chem. Ztg. 1908, **32,** 242; abst. Chem. Zentr. 1908, **79,** I, 1617), a loose combination of HCl and cellulose is more probable, especially in view of the colloidal character of cellulose.

retained an acid reaction and oxidizing properties (towards potassium iodide) even after exhaustive washing with distilled water. The acidity was removed or rather neutralized by washing with hard water but the iodide reaction persisted. On the other hand, the oxidizing property was rapidly destroyed by boiling with water or by treatment with an "antichlor." Dry heat at 100° also destroyed the "active oxygen" in the cloth but the fabric was distinctly tendered. Having regard for all these circumstances, the authors postulate the possibility of the formation of a peroxidized derivative of cellulose under certain conditions of the industrial bleaching process. H. Ditz,[1] referring to the above opinion as expressed by Cross and Bevan, calls attention to the fact that the same phenomenon is obtainable with an acid solution of a persulfate. This is accomplished by slowly heating cellulose for about one and one-half hours with acid ammonium persulfate up to a temperature of 80° and then gradually cooling. During this operation gas is evolved to an extent not observable in the absence of the cellulose. When the product is subsequently well washed with cold water it exhibits the same properties as the cellulose peroxide described by Cross and Bevan. Ditz is satisfied that the change is not due to the absorption of persulfate by the cellulose, for when the latter is heated with a persulfate solution at boiling point cellulose exerts a powerful action on the decomposition of the salt with the evolution of oxygen and carbon dioxide

[1] Chem. Ztg. 1907, **31**, 833, 844, 857; abst. J. Soc. Dyers Col. 1907, **23**, 316; C. A. 1907, **1**, 2941; Chem. Zentr. 1907, **78**, II, 1606; J. S. C. I. 1907, **26**, 988, 1026; J. C. S. 1907, **92**, i, 829; see also J. prakt. Chem. 1908, (2), **78**, 343; abst. J. C. S. 1908, **94**, i, 954; Chem. Zentr. 1907, II, 1606; 1908, II, 2000; J. C. S. 1908, i, 954; C. A. 1909, **3**, 841; Bull. Soc. Chim. 1909, **6**, 1176; Chem. Ztg. Rep. 1907, **31**, 833, 844, 857; 1908, **32**, 619; J. S. C. I. 1908, **27**, 1129; C. A. 1909, **3**, 841. He found (J. prakt. Chem. 1908, (2), **78**, 343; abst. Chem. Zentr. 1908, II, 2000; J. C. S. 1908, **94**, i, 954; C. A. 1909, **3**, 841; Bull. Soc. Chim. 1909, **6**, 1176) that very little gas is evolved by the action of hydrogen peroxide upon cellulose, with ammonium persulfate, the reverse is the case. It appears that cellulose peroxide formed by the persulfate method does not contain sulfuric acid. Cellulose peroxide does not evolve ammonia when boiled with lime water, but gives with Nessler's reagent a brown coloration, becoming grey in consequence of the reduction of the mercuric salt by the small amount of oxycellulose present in the peroxide. Due to the fact that it behaves towards Nessler's reagent in the same manner as a dilute formaldehyde solution, oxycellulose is considered to probably contain an aldehydic group. The gases evolved by the action of ammonium or potassium persulfate upon cellulose are found to contain carbon dioxide in addition to "active" oxygen. Compare L. Rosenthaler, Pharm. Central h. 1906, **47**, 581; abst. J. C. S. 1906, **90**, ii, 911; Chem. Centr. 1906, **77**, II, 717.

and an irritating gas, but in these circumstances the cellulose does not retain the properties of a peroxide. Again, when ammonium persulfate is allowed to act on cellulose in the absence of an acid, the products obtained show but very faintly the properties of a peroxide. This author lays some stress on the distinct difference between the acidity of the cellulose peroxide and the active oxygen, for the former is not destroyed, like the latter, by boiling with water for two or three minutes, and these two particular properties are quite independent of each other. On gently heating cellulose peroxide obtained by means of ammonium persulfate with a 10% solution of potassium hydroxide, a golden yellow coloration is produced, at the same time partial solution taking place. On treating and filtering with an excess of hydrochloric acid, almost total decoloration ensues with the formation of a dirty white deposit. The author finds a difference between the peroxidized cellulose under consideration and the hydralcellulose of Bumcke and Wolffenstein[1] obtained by the action of hydrogen peroxide on cellulose in so far as it contains an acid, possibly acid-cellulose. It has been shown that the products of the action of ammonium persulfate in the presence of sulfuric acid upon cellulose are a peroxide, and free acid, and only probably a portion of unaffected cellulose. Dilute sulfuric acid at 70° acting alone upon cellulose, yields a product containing traces of free acid and a reducing body. The latter has been found to be hydrocellulose, not oxycellulose. When ammonium persulfate is used alone, oxidized cellulose with a formation of oxycellulose and free acid results, but only traces of peroxidized cellulose. The author's conclusions are that the sulfuric acid exerts this influence by increasing velocity at the rate of decomposition of the ammonium persulfate. J. Heinke[2] has found that linen fiber once peroxidized, does not lose the property of liberating iodine from

---

[1] Ber. 1899, **32**, 2493; abst. J. C. S. 1899, **76**, i, 854; J. S. C. I. 1899, **18**, 940; Chem. Centr. 1899, **70**, II, 752; Jahr. Chem. 1899, **52**, 300, 1290; Bull. Soc. Chim. 1900, **24**, 620; Meyer Jahr. Chem. 1899, **9**, 300.

[2] Chem. Ztg. 1907, **31**, 974; abst. J. Soc. Dyers Col. 1907, **23**, 317; C. A. 1908, **2**, 180; Chem. Zentr. 1907, **78**, II, 1714; Jahr. Chem. 1905–1908, II, 961. He was able to confirm the observations of Cross and Bevan in the case of bleached linen, where an iodine reaction persists in spite of the most thorough washing. Heinke points out that the dry material is to all appearance not damaged during exposure as regards decrease in tensile strength, but a loss of strength in the material up to 50% was found to take place on boiling it in alkaline solutions.

potassium iodide by drying above the normal temperature, and shows according to the author's rather limited experimentation, no appreciable weakening of the fiber; but on the other hand, if the same material be treated in a warm weak solution of alkali such as sodium carbonate, sodium hydroxide or sodium sulfide, then the fiber and the linen become quite yellowish, while the fiber loses at the same time about 50% in strength and is useless for weaving purposes. From the investigations hitherto recorded, it would appear that the amount of "cellulose peroxide" formed is in any case extremely small.

As stated, according to C. Doree,[1] much more cellulose peroxide is formed by the action of ozone from air-dry than from bone-dry cellulose product. The "active oxygen" fixed by air-dry cotton, mercerized cotton and lustracellulose on eighteen hours' exposure to ozone was 0.0056%, 0.0106% and 0.0248%, respectively. The peroxide slowly decomposes, the formation of hydrogen peroxide on treatment with water being partially decomposed by two hours heating at 37° and almost entirely so when the temperature is raised to 95°. The activity is retained some weeks when exposed in a dry atmosphere.

However, M. Cunningham and C. Doree[2] have found that 1% to 2% ozone rapidly attacks cotton, forming a cellulose peroxide and an acid derivative, together with some carbon dioxide, the peroxide content being decomposed at 80° C. The acid may be removed by boiling with water or by digestion with decinormal alkali, the neutral fiber residue then obtained being an oxycellulose.

With lignocellulose jute no appreciable effect is observed unless water is present, in which case it is oxidized giving carbon dioxide, acetic and formic acids and complex non-volatile acids that yield furfural. Quantitative measurements of the progressive action of the ozone shows that the lignone group is rapidly attacked in the first three hours, after which the action becomes slower, the residue then being oxidized uniformly. The lignin

---

[1] Proc. Chem. Soc. 1913, **29**, 222; abst. J. S. C. I. 1913, **32**, 695; C. A. 1913, **7**, 2385. J. C. S. 1913, **103**, 1347; C. A. 1913, **7**, 3661. Chem. Zentr. 1913, **84**, II, 1466.

[2] Proc. Chem. Soc. 1912, **28**, 38; abst. J. S. C. I. 1912, **31**, 278; J. C. S. 1912, **101**, 497; Chem. Zentr. 1912, I, 1818; C. A. 1912, **6**, 1849; Bull. Soc. Chim. 1912, **12**, 1129.

reactions, however, cease when the loss of weight is about 33%.

Cellulose and Oxidizing Agents.[1] Although as has been previously stated, cellulose is unusually stable against oxidation and hydrolytic treatments considering the complexity of its composition, it is nevertheless profoundly changed upon prolonged exposure to these influences, especially at elevated temperatures.

In general, chlorine acts but slowly upon the fiber in the absence of moisture, although, as noted by J. Kolb,[2] dyed fibers are usually not discolored, although the cellulose may be rendered brittle and friable. It would appear that Kolb had not succeeded in entirely excluding moisture, his observations indicating hydrocellulose formation, this taking place as pointed out by Girard in the presence of moist hydrochloric acid.

G. Hertel has developed chlorine from bleaching powder and sulfuric acid and hung strips of cellulose in a current of the gas. The bleaching was found to be very effective when the chlorine was freshly generated but when the gas was left standing for some time it became quite ineffective, due most probably to the development of chlorine oxides. While freshly developed HCl acts energetically, dilution with an inert gas as CO_2 materially inhibits the action.[3]

When a strip of moist calico is hung in an atmosphere of chlorine mixed with air, G. Witz[4] observed that after a short time a much stronger dyeing effect with methylene blue was produced, oxycellulose ultimately being formed. T. Leykauf,[5] and subsequently Loewenthal[6] and C. Cross, and E. Bevan[7]

[1] Data in this topic has been taken from the excellent work of Schwalbe, "Die Chemie der Cellulose," to which source acknowledgment is due.

[2] Bull. Soc. Ind. Mulhouse, 1868, **38**, 914; Compt. rend. 1868, **66**, 1024; **67**, 742; Instit. 1868, 329; Ann. Chim. Phys. 1868, (4), **14**, 348; Bull. Soc. Chim. 1868, **9**, 431; Dingl. Poly. 1868, **190**, 62; 1869, **191**, 321; Jahr. Chem. 1868, **21**, 981.

[3] Leipziger Färberztg, 1886.

[4] Bull. soc. ind. Rouen, 1882, **10**, 439; 1883, **11**, 176; abst. J. S. C. I. 1883, **2**, 378; Mon. Sci. 1883, **25**, 517; 1884, **26**, 116; Dingl. Poly. 1883, **250**, 271; Jahr. Chem. 1883, **36**, 1782; Wag. Jahr. 1883, **29**, 1068; Färb. Must. Ztg. **17**, 129.

[5] J. prakt. Chem. 1840, **21**, 316. Leuch's Allg. polytech. Ztg. Sept. 1840. For data on some natural oxycelluloses, see G. de Chalmot, Ber. 1894, **27**, 1489; Am. Chem. J. 1894, **16**, 589; abst. J. C. S. 1894, **66**, i, 399; Bull. Soc. Chim. 1895, **14**, 271; Chem. Centr. 1894, II, 148; Jahr. Chem. 1894, **47**, 1146; Meyer Jahr. Chem. 1894, **4**, 570.

[6] Leipziger Monatsh. Textilind. 1890, 599.

[7] J. S. C. I. 1890, **9**, 450; Mon. Sci. 1891, **37**, 156; abst. Ber. 1891, **24**,

together with C. Schwalbe,[1] found that cellulose is chlorinated by chlorine, being still able to find chlorine in the cellulose after washing and exposing to the air for several months. Whether the chlorine absorption is in the cellulose or in the accompanying pectinous and nitrogenous protoplasmic material is not quite clear.

However, G. Witz[2] has convincingly demonstrated that the change in the cellulose fiber is not entirely due to chlorination, for samples of chlorine-impregnated calico, after saturating with nitric acid, drying and igniting, gave no indications of the presence of chlorine.

In the experience of A. Franchimont,[3] bromine in the absence of moisture, does not act upon cellulose, a chloroform solution of bromine being without action. The necessity, however, should be emphasized of the absence of moisture, otherwise HBr will be formed, and this in turn, results in the formation of hydrocellulose and brom-methylfurfurol. So also when HBr is formed from the bromine, oxidation by the nascent oxygen must also take place, as in the case with chlorine. If, however, as stated by O. Faber and B. Tollens,[4] large amounts of bromine are allowed to act upon cellulose in the presence of water, especially in the presence of calcium carbonate, a typical oxycellulose results.

Iodine appears to be devoid of oxidizing action, although it is absorbed by the cellulose. J. Huebner[5] has recorded that 10 gm. cotton takes up from a solution of 7.6 gm. iodine in 750 cc. KI solution, 0.136 gm. iodine, which, however, may be readily and completely removed by energetic washing. Filter paper undoubtedly has a strong absorbent power for iodine, and accord-

---

R, 621; Chem. Centr. 1890, **61**, II, 185; Chem. Tech. Rep. 1890, **29**, I, 89; Chem. Ztg. Rep. 1890, **14**, 216; Jahr. Chem. 1890, **43**, 2886; Tech. Chem. Jahr. 1890–1891, **13**, 521; Wag. Jahr. 1890, **36**, 1110; Deutsche Chem. Ztg. 1890, 220.

[1] Chem. Ztg. 1908, **32**, 489, 521.

[2] Bull. soc. ind. Rouen, 1882, **10**, 446.

[3] Rec. trav. Chim. Pays-Bas, 1883, **2**, 91; abst. Ber. 1883, **16**, 1872; Jahr. Chem. 1883, **36**, 1366.

[4] Ber. 1899, **32**, 2591; abst. J. S. C. I. 1899, **18**, 1014; J. C. S. 1899, **76**, i, 854; Chem. Centr. 1899, **70**, II, 901; Jahr. Chem. 1899, **52**, 1292; Chem. Ztg. Rep. 1899, **23**, 321; Chem. Tech. Rep. 1899, **38**, 550; Bull. Soc. Chim. 1900, **24**, 621.

[5] J. C. S. 1907, **91**, 1072; Proc. Chem. Soc. 1907, **23**, 144; Chem. News, 1907, **95**, 273; abst. J. S. C. I. 1907, **26**, 866; Bull. Soc. Chim. 1908, (4), **4**, 165; Rep. Chim. 1907, **7**, 355; Chem. Zentr. 1907, **78**, II, 752; Chem. Ztg. 1907, **31**, 716; Jahr. Chem. 1905–1908, II, 3171.

ing to F. Mylius[1] forms a loose chemical combination with cellulose similar to that with starch. Cellulose free from starch is stained yellow to brown with iodine, but with zinc iodide or iodine in H_2SO_4 a strong blue color appears. E. Flechsig[2] contends that this coloration appears only in the presence of acid.

As an oxidizing agent for cellulose, oxygen in the entire absence of light is negative, as well preserved manuscripts from very ancient times prove. With ozone there is no analogy, for the latter acts very energetically upon cellulose at the same time increasing its weight as pointed out by J. Kolb,[3] who exposed unbleached dry linen yarn for some weeks to the influence of a current of ozone produced by the action of sulfuric acid upon potassium permanganate. G. Witz[4] has also demonstrated the oxidizing action of ozone by dyeings with methylene blue (oxycellulose formation). High concentrations of hydrogen dioxide according to G. Bumcke and R. Wolffenstein[5] induce energetic hydrolysis. With elevated temperatures, however, oxidizing action takes place, Prud'homme[6] having recorded the ready formation of oxycellulose upon boiling cellulose in the presence of magnesia with concentrated hydrogen dioxide solutions.

Certain metals and metallic oxides seem to markedly intensify the action of hydrogen dioxide upon cellulose, the oxides of iron,

---

[1] Ber. 1895, **28**, 390; abst. J. C. S. 1895, **68**, i, 313; Bull. Soc. Chim. 1895, **14**, 901; Chem. Centr. 1895, **66**, I, 793; Jahr. Chem. 1895, **48**, 514.

[2] Zts. Physiol. Chem. 1883, **7**, 523; abst. Zts. deutsche Spiritusfabr. 1883, 805; Ber. 1883, **16**, 2508; Chem. Tech. Rep. 1883, **22**, II, 144; Tech. Chem. Jahr. 1883–1884, **6**, 275; Jahr. Chem. 1883, **36**, 1363; Wag. Jahr. 1883, **29**, 681.

[3] Bull. Soc. Ind. Mulhouse, 1868, **38**, 914; Compt. rend. 1868, **66**, 1024; **67**, 742; Ann. Chim. Phys. 1868, (4), **14**, 348; Bull. Soc. Chim. 1869, **11**, 431; abst. Dingl. Poly. 1868, **190**, 62; 1869, **191**, 321; Jahr. Chem. 1868, **21**, 981.

[4] Bull. soc. ind. Rouen, 1883, **11**, 198; abst. J. S. C. I. 1883, **2**, 378; Jahr. Chem. 1883, **36**, 1782; Wag. Jahr. 1883, **29**, 1068.

[5] Ber. 1899, **32**, 2493; abst. J. C. S. 1899, **76**, i, 852; J. S. C. I. 1899, **18**, 940; Bull. Soc. Chim. 1900, **24**, 620; Chem. Centr. 1899, II, 752; Jahr. Chem. 1899, **52**, 1290; Meyer Jahr. Chem. 1899, **9**, 300.

[6] Bull. Soc. Ind. Mulhouse, 1891, **61**, 503; Faerb. Ztg. 1891–1892, 12; Compt. rend. 1891, **112**, 1374; Mon. Sci. 1891, **38**, 677; 1892, **39**, 495; abst. Chem. News, 1891, **64**, 9; J. C. S. 1891, **60**, 1447; J. S. C. I. 1891, **10**, 834; Bull. Soc. Chem. 1892, **7**, 79; Rev. gén. sci. 1891, **2**, 455; Ber. 1891, **24**, R, 595; Chem. Centr. 1891, **62**, II, 685; Chem. Tech. Rep. 1891, **30**, II, 123; Chem. Ztg. Rep. 1891, **15**, 1024; Jahr. Chem. 1891, **44**, 2816; Wag. Jahr. 1891, **37**, 1115; Zts. ang. Chem. 1892, **5**, 718; Tech. Chem. Jahr. 1891–1892, **14**, 491; Indbl. 1891, 262; Deutsche Chem. Ztg. 1891, 218.

aluminum and chromium appearing to act as catalysts. E. Knecht[1] mordanted cotton with chromium oxide, and upon treatment of the mordanted fabric with hydrogen dioxide, found oxycellulose readily formed. Wolffenstein[2] made similar observations with metals, specially lead.

Nitric acid may either form (a) hydrocellulose, (b) oxycellulose, (c) mercerize, or (d) nitrate. The oxides of nitrogen, however, appear to act entirely different. The gases from the action of acetic acid upon a metallic nitrite apparently do not form oxycellulose as judged by the methylene blue test,[3] but the fumes from concentrated nitric acid weaken cotton and other forms of cellulose.[4] Mitscherlich[5] affirms that Swedish filter paper is not attacked by HNO_3 of 1.2 sp. gr. in the cold. At more elevated temperatures oxycellulose is formed, as has been noted independently by several observers. Whether or not the reaction of oxycellulose formation by nitric acid is due to the presence of small amounts of nitrous acid, as assumed by B. Bull[6] for the oxidation of compound celluloses, has, as yet, not been proven.

Cellulose may also be oxidized with chromic acid, a fact long since known and made use of by calico printers. P. Jean-

---

[1] J. Soc. Dyers Col. 1897, **13**, 109, 131; abst. J. S. C. I. 1897, **16**, 534; Jahr. Chem. 1897, **50**, 1511. See also Persoz, Bull. soc. ind. Rouen, 1882, **10**, 466; Bull. Soc. Chim. 1883, **39**, 620; Chem. Ind. 1884, **7**, 162; Chem. Tech. Rep. 1884, **23**, I, 26.

[2] D. R. P. 206566; abst. Chem. Zentr. 1909, **80**, I, 957; Chem. Ztg. Rep. 1909, **33**, 152.

[3] G. Witz, Bull. soc. ind. Rouen, 1883, **11**, 212.

[4] A. Schuerer, Bull. Soc. Ind. Mulhouse, 1888, **55**, 304, 364, 399, 439; abst. J. S. C. I. 1888, **7**, 841, 843; Bull. Soc. Chim. 1888, **50**, 597; Mon. Sci. 1889, **33**, 257; Chem. Ind. 1888, **11**, 556; 1889, **12**, 40; Chem. Tech. Rep. 1888, **27**, II, 60, 105; Jahr. Chem. 1889, **42**, 2841; Wag. Jahr. 1888, **34**, 1099.

[5] Gmelin Handbuch der Chemie, **7**, 585.

[6] J. C. S. 1897, **71**, 1090; Chem. News, 1897, **76**, 249; abst. Chem. Centr. 1897, **68**, II, 733; Jahr. Chem. 1897, **50**, 1507; Meyer Jahr. Chem. 1897, **7**, 151. See also G. Mulder, Scheik. Onderzoek, 1846, **3**, 336; abst. Ann. 1846, **60**, 334; J. prakt. Chem. 1846, **39**, 150. C. Cross and E. Bevan, J. C. S. 1883, **43**, 22; Chem. News, 1882, **46**, 240; J. S. C. I. 1884, **3**, 206, 291; abst. Bull. Soc. Chim. 1883, **39**, 671; Chem. Ind. 1883, **6**, 353; Chem. Tech. Rep. 1883, **22**, II, 94; Dingl. Poly. 1883, **250**, 280; Jahr. Chem. 1883, **36**, 1366, 1777; Mon. prod. chim. 1883, 242. Sacc, Ann. Chim. Phys. 1849, (3), **25**, 218; 1892, **271**, 288. J. Porter, Pharm. Centr. 1849, **20**, 777; abst. Jahr. Chem. 1849, **2**, 474; Ann. 1849, **71**, 115. J. Lindsey and B. Tollens, Ann. 1892, **267**, 366. R. Tromp de Haas and B. Tollens, Ann. 1895, **286**, 296. G. Witz, Bull. soc. ind. Rouen, 1882, 416. A. Nastjukoff, Bull. soc. ind. Rouen, 1883, 169; 1892, 483. E. Nölting, Bull. soc. ind. Rouen, 1892, 493.

maire,[1] G. Witz[2] and C. Brandt[3] have all employed the formation of oxycellulose by means of chromic acid to produce dark designs on a light background in a one-bath operation. The oxycellulose obtained with chromic acid differs from the oxycellulose prepared by means of nitric acid in that the latter, upon distillation, yields much less furfurol than the former.

Alkaline solutions of chlorates appear[4] to be without action upon cellulose. Vignon used chlorates in acid solution for oxycellulose formation.

C. Brandt has observed[5] that aniline black may be prevented from turning green by over-dyeing with methyl violet,—green and violet being supplementary to blue. This peculiar property according to Witz, can only be explained upon the assumption that traces of oxycellulose are also formed.[6]

Hypochlorous acid is an energetic oxidizing agent for cellulose, it depending entirely upon the concentration of the bleaching liquor as to whether the cellulose is damaged.[7] The strength of bleaching solution for maximum effect without weakening the fiber is given as 0.2% by G. Witz,[8] and 0.8% by A. Nastjukoff.[9]

If cotton fabric is saturated with a strong sodium hypochlorite solution and subsequently placed in an atmosphere of CO_2, an exceedingly violent reaction takes place, as noted by A. Girard.[10] The fabric almost instantaneously loses its fibrous structure, swells up, and ultimately becomes a thick structureless paste. C.

---

[1] Bull. Soc. Ind. Mulhouse, 1873, **43**, 334; abst. Chem. News, 1874, **29**, 174; J. C. S. 1874, **27**, 931; Chem. Centr. 1874, **45**, 207; Chem. Tech. Rep. 1874, **13**, I, 70; Dingl. Poly. 1874, **211**, 403; Jahr. Chem. 1874, **27**, 1199; Wag. Jahr. 1874, **20**, 852; Indbl. 1874, 133; Poly. Centr. 1874, **40**, 144; Deutsche Ind. Ztg. 1874, 96; Poly. Notizbl. 1874, **29**, 85.

[2] Bull. soc. ind. Rouen, 1883, **11**, 208.

[3] Bull. Soc. Ind. Mulhouse, 1891, **61**, 496; abst. Reiman's Faerberztg. 1891, 3, 61, 62; Deutsche Chem. Ztg. 1891, 417; J. S. C. I. 1892, **11**, 33; Chem. Ind. 1892, **15**, 172; Chem. Tech. Rep. 1891, **30**, 63; Wag. Jahr. 1891, **37**, 1138.

[4] G. Witz, Bull. soc. ind. Rouen, 1883, **11**, 202.

[5] Bull. Soc. Ind. Mulhouse, 1876, **66**, 441; abst. Chem. Tech. Rep. 1876, **15**, I, 49; Dingl. Poly. 1877, **223**, 331; Tudbl. 1877, 191; Zts. Chem. Grossgew. 1876, **1**, 204.

[6] Bull. soc. ind. Rouen, 1883, **11**, 206.

[7] Dalichow, D. R. P. 135723. J. Thompson and J. Rickmann, D. R. P. 30830, 32704; abst. Wag. Jahr. 1885, **31**, 966.

[8] Bull. soc. ind. Rouen, 1882, **10**, 416.

[9] Bull. Soc. Ind. Mulhouse, 1892, **62**, 500.

[10] Ann. Chim. Phys. 1881, (5), **24**, 337, 382; abst. Jahr. Chem. 1881, **34**, 985; J. C. S. 1882, **42**, 378.

Schwalbe[1] has shown that inasmuch as the product possesses a high degree of reducing power, oxycellulose undoubtedly is present. A. Girard[2] contends that the destructive action of bleaching powder on cellulose is due to the formation of hydrocellulose—the CO_2 and hypochlorous acid forming HCl and this in turn producing hydrocellulose—a view also expressed by Dumas,[3] who assumed a transformation of the chlorine into HCl under the influence of light. In support of his contention, Girard immersed a piece of hemp fabric in sodium hypochlorite solution which retained its strength, but immediately disintegrated in an atmosphere of CO_2.[4]

Calcium hypochlorite is unquestionably the most important and widely used of the alkaline oxidizing agents for cellulose, and, as has been pointed out, it does appreciably attack the fiber in dilute solution, while with higher concentrations and at elevated temperatures oxycellulose is formed. At the temperature of boiling water disintegration is complete, and the cellulose becomes a structureless powder devoid of tensile strength. Bearing in mind that a sodium hypochlorite solution when heated with cellulose produces energetic oxidation, it is difficult to reconcile the statement of Salvetat and J. Barral[5] that no weakening of the fiber results upon saturating cellulose with sodium hypochlorite solution of 5° Bé. and subsequently heating to 140°.

The action of alkaline bromine solutions is presumably analogous to that of chlorine, J. Collie[6] having recorded that energetic action leads to the formation of bromoform among the reaction products along with carbon tetrabromide.

The action of potassium permanganate is different from the

[1] Zts. ang. Chem. 1907, **20**, 2171; Chem. Ztg. 1907, **31**, 937; abst. C. A. 1908, **2**, 704; J. C. S. 1908, **94**, i, 9; Bull. Soc. Chim. 1908, **4**, 381; Ber. 1907, **40**, 961, 4523; Chem. Zentr. 1908, **79**, I, 240; Jahr. Chem. 1905–1908, II, 961.

[2] Compt. rend. 1877, **81**, 1105; Ann. Chim. Phys. 1881, (5), **24**, 337, 382; abst. Jahr. Chem. 1881, **34**, 985; J. C. S. 1879, **36**, 911; 1882, **42**, 378.

[3] Traite de chimie, 1843, **6**, 31.

[4] According to Witz (Bull. soc. ind. Rouen, 1882, **10**, 440) the CO_2 of the air decomposes calcium hypochlorite into calcium carbonate and hypochlorous acid. This very unstable compound, with an odor entirely different from that of chlorine, further decomposes in the presence of organic matter.

[5] Ann. Chim. Phys. 1876, (5), **9**, 126; Chem. News, 1876, **33**, 18; abst. J. C. S. 1876, **29**, 821; Ber. 1876, **9**, 68; Compt. rend. 1875, **81**, 1189; Dingl. Poly. 1876, **219**, 469; Jahr. Chem. 1875, **28**, 1164; Bull. Soc. Chim. 1876, **25**, 425.

[6] J. C. S. 1894, **65**, 262; abst. Bull. Soc. Chim. 1894, **12**, 448; Jahr. Chem. 1894, **47**, 758.

other oxidizing agents above mentioned, G. Witz[1] having found that oxidation with permanganate, although resulting in the formation of a brilliant white color, nevertheless perceptibly weakened the cellulose fiber. While potassium ferrocyanide scarcely attacks cellulose,[2] potassium permanganate has been employed by E. Berl and R. Klaye[3] to prepare oxycellulose from cellulose.

Ammonium persulfate under certain circumstances, may cause considerable deterioration in the strength of cotton fiber as clearly shown by A. Scheurer,[4] where losses up to 40% have been recorded.

Oxycellulose. When powerful inorganic oxidizing agents such as chlorine, permanganates, chromic acid, chlorates and persulfates are allowed to act in concentrated solution upon various forms of cellulose, the latter is readily attacked and converted into a brittle modification which has an increased affinity for dyestuffs. In a fairly comprehensive manner. G. Witz[5] subjected the conditions of origin and properties of the converted cellulose, called "oxycellulose" by him, to a thorough investigation. He preferably prepares oxycellulose by immersing in a solution of chloride of lime or other liquid containing free chlorine, strips of cotton cellulose which are afterwards exposed to the air. No exterior change in the material is apparent even under vigorous oxidation, but it is found to be very brittle and friable and has

---

[1] Bull. soc. ind. Rouen, 1883, **11**, 211.

[2] Bull. Soc. Ind. Mulhouse, 1890, **60**, 311.

[3] Zts. Schiess u. Sprengw. 1907, **2**, 403; abst. C. A. 1908, **2**, 184; J. C. S. 1908, **94**, i, 504; J. S. C. I. 1907, **26**, 1157; Chem. Zentr. 1908, I, 1381; Chem. Ztg. Rep. 1908, **32**, 43; Jahr. Chem. 1905-1908, II, 976.

[4] Bull. Soc. Ind. Mulhouse, 1901, **71**, 182; abst. J. C. S. I. 1901, **20**, 891; Meyer Jahr. Chem. 1901, **11**, 447.

[5] Bull. Soc. Chim. Rouen, 1882, **10**, 416, 447; 1883, **11**, 169, 2210; abst. Wag. Jahr. 1883, **29**, 1068; J. C. S. 1884, **46**, 528; J. S. C. I. 1883, **2**, 378; Mon. Sci. 1883, **25**, 517; 1884, **26**, 1161; Dingl. Poly. 1883, **250**, 271; Jahr. Chem. 1883, **36**, 1782; Färb. Must. Ztg. **17**, 129. F. von Goppelsroeder alleges (Dingl. Poly. 1884, **254**, 42; Chem. Ind. 1884, **8**, 14; abst. Jahr. Chem. 1884, **37**, 1833, 1845; J. C. S. 1885, **48**, 208; J. S. C. I. 1884, **3**, 518, 519) that, in confirmation of the results of Witz and Schmidt, that when cotton saturated with a solution of potassium nitrate or chlorate or sodium chloride, either neutral or alkaline, is placed in contact with platinum foil and a current passed through, the cotton at the points touched by the positive wire have a greater affinity for certain dyes, just as though mordants had been applied, so that it was found possible to produce designs of a darker shade on a lighter background when dyeing with methylene blue, aniline green or fuchsine, Turkey red or indigo blue.

lost considerable of its strength when strong solutions of bleaching powder have been used. In this case the oxycellulose is obtainable as a clear, voluminous, water-insoluble powder.

The oxycellulose of Witz is quite free from chlorine, as shown by analysis. The structureless and brittle nature of oxycellulose caused a marked tendering of the cotton fiber when it is present in considerable quantities.

Oxycellulose as prepared by Witz is stable at 100° in vacuum, but exposed to dampness and air rapidly turns pale yellow, in which condition it is partially soluble in alkalis. The fabric, however, remains pale yellow and does not turn white as is the case when partially prepared oxycellulose is treated with alkalis or alkaline earths. When brought in contact with steam the yellow color gradually turns to a brown. If spots of oxycellulose have been formed during the bleaching operation they then turn brownish yellow if much oxycellulose is contained in them and the strength of the fabric suffers correspondingly. However, upon immersing oxycellulose in boiling water no change in color occurs, while the water remains colored. However, if a small amount of caustic soda is contained in the water, the yellowish brown color immediately appears and a similar weakening of the fabric results as when exposed to steam. By immersion in a boiling 5% solution of sodium hydroxide, a vivid yellow is immediately produced analogous to that of chromate solutions, this color being reproduced in a lesser degree by means of caustic soda. This phenomenon is not shown by treatment with ammonium hydroxide.

The reduction of alkaline copper tartrate (Fehling's solution) is most characteristic. After treatment with boiling caustic soda solution, the reducing power is considerably decreased, from which it appears that the reducing property is due to the presence of a substance or substances which can be extracted by alkalis. The hot alkaline extract, however, possesses a reducing power which rapidly disappears.

The affinity to hold basic dyestuffs, specifically methylene blue, either before or after the alkaline washing is very pronounced and characteristic, while with diphenylamine blue there is little or no attraction. With cold decinormal sodium hydroxide solution, the oxycellulose of Witz is but slightly colored. However, there, occurs an appreciable observable chemical action, because the solution becomes brown on boiling, while even on standing the original light amber color turns to brown in the course of a few days.

The addition of hydrochloric acid to the freshly prepared alkaline extract causes a precipitation of voluminous flakes which, after careful washing are readily dyed by a cold solution of basic dyestuffs as methylene blue, methyl violet or rhoduline heliotrope. It would appear therefore that a secondary or subsidiary substance accompanies the oxycellulose proper, this latter material being insoluble in boiling water, not discolored by ammonium, and destroyed by alkaline solutions. The Witz oxycellulose proper is insoluble in both weak and concentrated sodium hydroxide.

According to V. Zanotti[1] the shells of nuts contain compounds which yield xylose and dextrose, and whose constitution is very different from that of cotton cellulose. He found that when cellulose prepared from purified cotton wool was oxidized by (a) hydrochloric acid and potassium chlorate, (b) chromic and sulfuric acids, (c) potassium permanganate and sulfuric acid, "oxycelluloses" of the following compositions were obtained:

	a	b	c
Ash	0.15	0.50	0.30
Carbon	43.66	42.96	42.52
Hydrogen	6.60	6.52	6.56
Oxygen	49.74	50.52	50.92
Furfuraldehyde	0.80	3.05	1.90
Cellulose	45.20	26.05	39.92
Oxycellulose, by difference	54.80	73.95	60.08

Action of alkalis indicated that these substances are really mixtures of cellulose and hydrocellulose with their oxidation and decomposition products.

A. Franchimont[2] has examined the oxycellulose as submitted by Witz to the esterification process, but found that by treatment of cellulose with an equal weight of fused zinc chloride and four times its weight of acetic anhydride at a temperature somewhat

---

[1] Annuario Soc. Chim. Milano, 1899, I, 27; abst. J. C. S. 1899, **76**, i, 851; Chem. Centr. 1899, I, 1209; Jahr. Chem. 1899, **52**, 1288.

[2] Compt. rend. 1879, **89**, 712; abst. Bull. soc. ind. Rouen, 1882, **10**, 448; 1883, **11**, 230; Rec. Trav. Chim. 1883, **2**, 239.

above one hundred degrees, a reaction occurs and the oxycellulose dissolves. Upon pouring this solution into a large volume of water, the ester precipitated out in amorphous white flakes. When washed with water until neutral and dried at a moderate temperature it has been found that cold alcohol dissolves from it a substance having a semblance to impure oct-acetyl-diglucose; while under the influence of heat a portion dissolves which is redeposited upon cooling. By exhaustion with boiling amyl alcohol, the latter also dissolves a portion which is re-precipitated upon cooling. The greater portion, however, is insoluble in this or other solvents but is soluble in highly concentrated acetic acid. The product of maximum esterification, when dried presents the same physical phenomena as the acetyl-celluloses obtained by the process of Schuetzenberger; i. e., the ability of transforming into a strong jelly when dissolved under heat in a comparatively large quantity of nitrobenzene and then allowed to cool.

G. Witz[1] has observed that oxycellulose exerts a powerful attraction for certain inorganic compounds and has proven that vanadium in the form of chloride may be withdrawn by oxycellulose from aqueous solutions containing some microscopic proportion, as one-billionth of the element.

The investigations of Witz also lead to the assumption that oxycellulose arises from cellulose by the direct admission of oxygen but no proof was given for the homogeneity of the cellulose operated upon and as shown by Witz, the oxycelluloses obtained by him by different processes were not identical, especially diverging in their composition as found upon analysis, from 42%–44.2% carbon.

The formation of oxycellulose, according to the microscopic

---

[1] Bull. soc. ind. Rouen, 1882, **10**, 416; abst. Dingl. Poly. 1883, **250**, 271; Jahr. Chem. 1883, 1782; G. Witz and F. Osmond (Bull. Soc. Chim. 1886, **45**, 309; abst. J. C. S. 1886, **50**, 923; Bull. soc. ind. Rouen, 1886, **14**, 30; J. S. C. I. 1886, **5**, 546; Ber. 1886, **19**, 318; Jahr. Chem. 1886, **39**, 1493; Wag. Jahr. 1886, **37**, 362) employ oxycellulose to detect and determine vanadium quantitatively in small traces, claiming a sensitiveness of one-millionth mgm. per liter. The test is performed by immersing strips of oxycellulose in the solution containing the vanadium salt for 8 hours at 15°. The strips are then washed, dried at 40°, and printed with the usual aniline black mixture, to which however, no vanadium compound has been added. The color is then developed in the oxidation chamber during a given period and the amount of vanadium in the solution examined is estimated by the depth of black obtained. The presence of 0.5–1 cc. of a mineral acid, as also the presence of ammonium oxalate entirely prevents the fixation of vanadium on the fiber.

investigations of Vetillart,[1] as shown by diminution of the width and length of fibers showed an average extent of 12.5%. While according to Permetier[2] the oxidized fibers do not swell up like ordinary cotton when brought in contact with cuprammonium solutions.

According to L. Vignon[3] oxycellulose may be prepared by treating purified cotton with a boiling solution of one per cent.

---

[1] Bull. soc. ind. Rouen, 1883, **11**, 234. The process of C. Kellner, (E. P. 5420, 1890; 24542, 1902. F. P. 326313. U. S. P. 773941, 1904; abst. J. S. C. I. 1890, **9**, 821; 1903, **22**, 817; 1904, **23**, 1159) is very similar to that of A. Nodon, (F. P. 453111. Belg. P. 253427, 1913. D. R. P. 251258; abst. Rev. Chim. Ind. 1913, **24**, 263; C. A. 1913, **7**, 310; Wag. Jahr. 1912, **58**, II, 634; Chem. Zentr. 1912, **83**, II, 1321; Chem. Ztg. Rep. 1912, **36**, 587; Ztg. ang. Chem. 1912, **25**, 2512; Kunst. 1912, **2**, 379) who preserves and strengthens cellulosic materials by an electric treatment in the presence of saline solutions. The material is only superficially saturated with the solution, the current being passed for a long time that the action may penetrate to the center. Aqueous solutions of sodium sulfate, sodium chloride or zinc chloride are specified.

[2] Bull. soc. ind. Rouen, 1883, **11**, 236. C. Smith, J. C. S. 1894, **65**, 472; Chem. News, 1894, **69**, 236; abst. J. S. C. I. 1894, **13**, 537; Ber. 1894, **27**, R, 513; Chem. Centr. 1894, **65**, I, 1152; Chem. Ztg. 1894, **18**, 674; Jahr. Chem. 1894, **47**, 1133; Meyer Jahr. Chem. 1894, **4**, 570; Jahr. organ. Chem. 1894, **2**, 220, has contributed interesting observations upon the "celluloses" of esparto and the cereal straws, and the (1) ultimate composition, and (2) amount of furfural obtained on boiling with aqueous HCl (1.06 relative density) determined. These "celluloses" are considered by the author to be oxycelluloses, and as they are widely distributed in nature, their physiology was studied. A systematic course of observations was therefore undertaken on the germination and growth of the barley plant in relation to the composition and constitution of its permanent tissue. The observation has been made that, by germination in the dark and growth of the sprouts (etiolated) until the endosperm is nearly exhausted, there is considerable increase in furfural-yielding constituents with no pentosan reaction, which was considered proof of the presence of oxycellulose.

[3] Compt. rend. 1897, **125**, 448; Bull. Soc. Chim. 1898, **19**, 790; abst. Chem. News, 1897, **76**, 194; J. C. S. 1898, **74**, i, 8; J. S. C. I. 1897, **16**, 908; 1898, **17**, 917; Mon. Sci. 1897, **49**, 859; Rev. Phys. Chim. 1897–1898, **2**, 21; Chem. Centr. 1897, **68**, II, 843; Chem. Ztg. 1897, **21**, 811; Jahr. Chem. 1897, **50**, 1506.

Compt. rend. 1898, **126**, 1658; Bull. Soc. Chim. 1898, **19**, 857; abst. Chem. News, 1898, **78**, 146; J. C. S. 1898, **74**, i, 619; J. S. C. I. 1898, **17**, 794; Mon. Sci. 1898, **51**, 527; Chem. Centr. 1898, **69**, II, 1246; Jahr. Chem. 1898, **51**, 1378.

Compt. rend. 1898, **127**, 872; Bull. Soc. Chim. 1899, **21**, 597; Chem. News, 1899, **79**, 35, J. C. S. 1899, **76**, i, 242; J. S. C. I. 1899, **18**, 81; Mon. Sci. 1899, **53**, 75; Rev. Chim. 1899, **1**, 132, 338; Rev. Phys. Chim. 1899, **3**, 80; Chem. Centr. 1899, **70**, I, 24; Chem. Ztg. 1898, **22**, 1049; Jahr. Chem. 1898, **51**, 1378. Compt. rend. 1899, **128**, 1038; Bull. Soc. Chim. 1899, **21**, 600; abst. Chem. News, 1899, **79**, 240; J. C. S. 1899, **76**, i, 560; J. S. C. I. 1899, **18**, 579; Rev. Chim. 1899, **1**, 293, 338; Rev. Phys. Chim. 1899, **3**, 27; Chem. Centr. 1899, **70**, I, 1162; Chem. Ztg. 1899, **23**, 404; Jahr. Chem. 1899, **52**, 1294.

Compt. rend. 1900, **131**, 509; Bull. Soc. Chim. 1901, **25**, 130; abst.

potassium hydroxide, then a one per cent. solution of hydrochloric acid in the cold followed by final treatment in a cold sodium carbonate solution. The fiber thus obtained is treated with hot 5% aqueous potassium chlorate to which a small amount of hydrochloric acid has been added, the liquid then being heated for an hour and the modified cotton thus obtained dried. The oxycellulose is obtained in the form of short brittle fibers which turn yellow upon heating.

Hemp was treated with two successive baths of one per cent. sodium carbonate for 30 minutes at the boiling temperature, followed by one per cent. caustic soda under the same conditions, the material being dissolved to a blackish liquid which when treated with hydrochloric acid, then water, and finally with alcohol and dried at 70° to 80°, produced a relatively white and brilliant, flocculent product. It was found that purified hemp was much more difficultly attacked than cotton when subjected to oxidation. In the oxidation of flax and ramie, both of these textiles behaved similar to cotton and gave a yield of 65%-75%. The four oxycelluloses thus produced by him were found to react strongly with Pasteur's liquid and in the fixation of basic coloring

Chem. News, 1900, **82,** 169; J. C. S. 1900, **78,** i, 589; J. S. C. I. 1900, **19,** 1039; Mon. Sci. 1900, **55,** 782; Rep. Chim. 1901, **1,** 102, 130; Rev. Phys. Chim. 1900, **4,** 467; Chem. Centr. 1900, **71,** II, 811; Jahr. Chem. 1900, **53,** 849.

Compt. rend. 1900, **131,** 530; Bull. Soc. Chim. 1901, **25,** 133; abst. Chem. News, 1900, **82,** 169; J. C. S. 1900, **78,** i, 629; J. S. C. I. 1900, **19,** 1045; Mon. Sci. 1900, **55,** 782; Chem. Centr. 1900, **71,** II, 811, 891; Chem. Ztg. 1900, **24,** 819, 847; Jahr. Chem. 1900, **53,** 849; Meyer Jahr. Chem. 1900, **10,** 321.

Compt. rend. 1900, **131,** 558; Bull. Soc. Chim. 1901, **25,** 135; abst. Chem. News, 1900, **82,** 208; J. C. S. 1900, **78,** i, 628; J. S. C. I. 1900, **19,** 1102; Mon. Sci. 1900, **55,** 784; Rep. Chim. 1901, **1,** 103, 130; Chem. Centr. 1900, **71,** II, 948; Chem. Ztg. 1900, **24,** 905; Jahr. Chem. 1900, **53,** 844. Compt. rend. 1900, **131,** 708; Bull. Soc. Chim. 1901, **25,** 137; abst. Chem. News, 1900, **82,** 255; J. C. S. 1901, **80,** i, 16; J. S. C. I. 1900, **19,** 1103; Mon. Sci. 1900, **55,** 835; Rep. Chim. 1901, **1,** 130; Chem. Centr. 1900, **71,** II, 1151; Chem. Ztg. 1900, **24,** 999; Jahr. Chem. 1900, **53,** 840. Compt. rend. 1903, **136,** 818; Bull. Soc. Chim. 1903, **21,** 509, 511; abst. Chem. News, 1903, **87,** 227; J. C. S. 1903, **84,** i, 461; J. S. C. I. 1903, **22,** 646; Mon. Sci. 1903, **59,** 380; Chem. Centr. 1903, **74,** I, 1081; Chem. Ztg. 1903, **27,** 372, 392; Jahr. Chem. 1903, **56,** 1017.

Compt. rend. 1903, **136,** 969; Bull. Soc. Chim. 1903, **29,** 513; abst. Chem. News, 1903, **87,** 251; J. C. S. 1903, **84,** i, 461; J. S. C. I. 1903, **22,** 646; Mon. Sci. 1903, **59,** 444; Chem. Centr. 1903, **74,** I, 1176; Chem. Ztg. 1903, **27,** 437; Jahr. Chem. 1903, **53,** 1014. L. Vignon and F. Gerin, Compt. rend. 1900, **131,** 588; Bull. Soc. Chim. 1901, **25,** 139; abst. Chem. News, 1900, **82,** 219; J. C. S. 1900, **78,** i, 629; J. S. C. I. 1900, **19,** 1103; Mon. Sci. 1900, **55,** 833; Rep. Chim. 1901, **1,** 103, 130; Chem. Centr. 1900, **71,** II, 1069; Chem. Ztg. 1900, **24,** 932; Jahr. Chem. 1900, **53,** 843.

materials Vignon has determined the absorbing power of the oxycelluloses with respect to safranin and methylene blue. He concludes that oxycellulose obtained from the oxidation of cotton, hemp, flax and ramie gives substantially the same products upon oxidation, the numerous discrepancies between the qualities of the oxycelluloses being relatively small and explained away either by the condition of the physical state characteristic to every textile material, or by the condensations of the molecule $(C_6H_{10}O_5)n$, which varies greatly in the different textile materials.

The oxycellulose of Vignon, when treated with potassium hydroxide solution is partially dissolved, giving a golden yellow solution. When dried at the ordinary temperature, a white, amorphous powder results containing 3.5% of water, which it loses at 110°. It has the same composition as cellulose, but differs from it in heat of combustion and in the ease with which it forms furfuraldehyde. It is soluble to the extent of 0.396 gm. per liter in hot water, and is insoluble in alcohol, ether, chloroform, benzene, acetone or CS_2. The yellow solution upon treatment with alkalis readily becomes brown upon standing, and may be re-precipitated by acids or solutions of the chlorides of potassium, sodium, barium or calcium. Hydrochloric acid dissolves it partially, nitric acid completely, and it is carbonized by sulfuric acid. Fehling's solution is reduced, and a pink coloration is given with Schiff's reagent.

I. Frankenburg and C. Weber[1] prepare α-oxycellulose by scouring cotton waste with 2.5% caustic soda, then immersing in a bleaching solution of sp. gr. 1.03. After 12 hours the cotton is removed, washed in acidulated water and finally disintegrated by treatment with a boiling solution of 20% hydrochloric, sulfuric or oxalic acids, or by impregnation with strong solutions of aluminium, magnesium or zinc chlorides, with subsequent steaming.

A patent was issued in 1887 to C. Lundholm and J. Sayers[2]

---

[1] E. P. 12367, 1893; abst. J. S. C. I. 1894, **13,** 725. D. R. P. 77826; abst. Chem. Ztg. 1894, **18,** 2044; Wag. Jahr. 1894, **40,** 1096. R. Alder (Can. P. 154062, 1914; abst. C. A. 1914, **8,** 2269) has described a plastic composite of ammonia, an albuminous substance and oxycellulose.

[2] E. P. 6399, 1889; abst. Wag. Jahr. 1890, **36,** 546; J. S. C. I. 1890, **9,** 414. L. Lloyd, J. Soc. Dyers Col. 1910, **26,** 273; abst. J. S. C. I. 1910, **29,** 1450; J. v. Falkenstein and A. Boehm (E. P. 7238, 1892; abst. J. S. C. I. 1893, **12,** 547; Chem. Ztg. 1893, **17,** 1417; Chem. Tech. Rep. 1893, **32,** II, 272.

for employment, —instead of nitrocellulose for the manufacture of explosives—the α-oxycellulose of Cross and Bevan. Their explosive comprises a combination of nitrated oxycellulose, either alone or mixed with an oxidizing agent, and with or without any carbonaceous matter or camphor in a suitable solvent for consolidating the explosive, the camphor being subsequently partially removed from the explosive.

B. Tollens[1] has shown that both hydrocellulose and all crude oxycellulose preparations contain unaltered cellulose. From the action of alkalis upon these bodies Tollens concludes that the true products of reaction (e. g. celloxin) are combined with the cellulose somewhat after the manner of esters. The author divides the cellulose group, therefore, into four classes:

(a) Celluloses.

(b) Hydrated Celluloses, i. e., hydrocelluloses and hemicelluloses, bodies which are non-reducing, but readily hydrolyzed to reducing compounds.

(c) Celluloses with acid, i. e., carboxyl groups; this class including the pectins.

(d) Celluloses with both acid (carboxyl) groups and aldhydic or ketonic groups; this class including the oxycelluloses which are cupric reducing bodies.

The more highly oxidized classes, "c" and "d" are distinguishable from "a" and "b" by elementary analysis, the ratio of H and O being 1:8 to 9 instead of 1:8 as in the "a" and "b" classes.

O. v. Faber and B. Tollens[2] have examined oxycellulose prepared in various manners by heating with milk of lime for

---

D. R. P. 70067; abst. Ztg. ang. Chem. 1893, **6**, 465; Chem. Centr. 1893, **64**, II, 1015; Chem. Ztg. 1894, **18**, 1089; Chem. Tech. Rep. 1893, **32**, 272; Wag. Jahr. 1893, **39**, 426; Ber. 1893, **26**, 958. Jahr. organ. Chem. 1893, **1**, 262; Tech. Chem. Jahr. 1893–1894, **16**, 165; Meyer Jahr. Chem. 1893, **3**, 366, prepare nitrocellulose for smokeless powder from cellulose which has been oxidized to oxycellulose by treatment with potassium permanganate and nitric acid, which also renders the nitrocellulose amorphous.

[1] Ber. 1901, **34**, 1434; abst. J. S. C. I. 1901, **20**, 740; J. Soc. Dyers Col. 1901, **17**, 238; J. C. S. 1901, **80**, i, 453; Bull. Soc. Chim. 1902, **28**, 269; Chem. Centr. 1901, **72**, II, 39; Jahr. Chem. 1901, **54**, 897.

[2] Ber. 1899, **32**, 2589; abst. J. S. C. I. 1899, **18**, 1014; J. C. S. 1899, **76**, i, 854; Jahr. Chem. 1899, **52**, 1292; Chem. Ztg. Rep. 1899, **23**, 321; Chem. Tech. Rep. 1899, **38**, 550; Bull. Soc. Chim. 1900, **24**, 621. For natural oxycelluloses, consult G. de. Chalmot, Amer. Chem. J. 1894, **16**, 589; Ber. 1894, **27**, 1489; J. C. S. 1894, **66**, i, 399; Bull. Soc. Chim. 1895, **14**, 271; Chem. Centr. 1894, **65**, II, 148; Jahr. Chem. 1894, **47**, 1146; Meyer Jahr. Chem. 1894, **4**, 570; Jahr. organ. Chem. 1894, **2**, 221.

several hours on the water bath. In this way the oxidized portion of the product, termed by them "celloxin," was broken down into soluble products from which isosaccharic acid and dihydroxybutyric acid were separated with calcium salts.

J. Murumow, J. Sack and B. Tollens[1] have extended and expanded this series of observations to an oxycellulose prepared by the addition of potassium chlorate and hydrochloric acid according to the method of Vignon, and have found that the soluble products are identical in this case with those isolated by Faver and Tollens, and the insoluble residue likewise possessed all the properties of unaltered cellulose.

A. Nastukoff[2] has oxidized Swedish filter paper with (1) calcium hypochlorite solution,[3] (2) permanganate solution followed after 36 hours by the introduction of sulfur dioxide gas and finally the addition of weak and lukewarm sulfuric acid. The products in both cases appeared to be laevo-oxycelluloses. By heating these on the water bath with ten volumes of sulfuric acid solution of 5%, washing and reheating with a similar volume of 10% sodium carbonate solution, a new class of oxycelluloses characterized by ready solubility in water were obtained in 60–

---

1. Ber. 1901, **34**, 1427; abst. J. S. C. I. 1901, **20**, 739; J. Soc. Dyers Col. 1901, **17**, 238; J. C. S. 1901, **80**, i, 453; Bull. Soc. Chim. 1902, **28**, 269; Chem. Centr. 1901, **72**, II, 38; Jahr. Chem. 1901, **54**, 896. J. Porter, Pharm. Centr. 1849, **20**, 777; Ann. 1849, **71**, 115; Amer. J. Sci. (Sill.), 1850, (2), **9**, 20; Chem. Gaz. 1849, 469; Jahr. Chem. 1849, **2**, 474. S. Zeisel and M. Stritar, Ber. 1902, **35**, 1252; abst. J. C. S. 1902, **82**, ii, 363; J. S. C. I. 1903, **22**, 642; Bull. Soc. Chim. 1902, **28**, 863; Rep. Chim. 1902, **2**, 408; Chem. Centr. 1902, **73**, I, 1076; Chem. Ztg. Rep. 1902, **26**, 124; Jahr. Chem. 1902, **55**, 1052; Zts. ang. Chem. 1902, **15**, 736. B. Bull, J. C. S. 1897, **71**, 1090; Chem. News, 1897, **76**, 249; abst. Chem. Centr. 1897, **68**, II, 733; Jahr. Chem. 1897, **50**, 1507; Meyer Jahr. Chem. 1897, **7**, 151.

2. J. Russ. Phys. Chem. Soc. 1900, **32**, 543; 1901, **33**, 310, 678; Ber. 1900, **33**, 2239; 1901, **34**, 719, 3589; abst. Chem. News, 1902, **86**, 306; J. C. S. 1900, **78**, i, 540; J. S. C. I. 1900, **19**, 733; 1901, **20**, 63, 573; J. Soc. Dyers Col. 1901, **17**, 122; Bull. Soc. Chim. 1901, **26**, 123, 557; 1902, **28**, 130, 481; Rep. Chim. 1901, **1**, 414; 1902, **2**, 189; Chem. Centr. 1900, **71**, II, 430; 1901, **72**, I, 99, 932; II, 335, 1263; Chem. Ztg. Rep. 1900, **24**, 258; 1901, **25**, 122, 353; Jahr. Chem. 1900, **53**, 844; 1901, **54**, 897, 898; Meyer Jahr. Chem. 1901, **11**, 441; Zts. ang. Chem. 1900, **13**, 1083.

3. H. Moore (J. Soc. Dyers Col. 1915, **31**, 180; abst. J. S. C. I. 1915, **34**, 1008; C. A. 1915, **9**, 3365) has also studied the action of calcium and sodium hypochlorite of varying concentration upon cotton yarn, methylene blue being employed to estimate the amount of oxycellulose formed. The effect of moderate additions of acid was to decrease the amount of oxycellulose and not increase it, as might reasonably be expected. Upon addition of alkali to the bleach, a minimum amount of oxycellulose is produced at a definite concentration of caustic soda. Permanganate solutions gave similar results.

80% yield. The oxycellulose resulting from the action of the chloride of lime required to be heated with acid for three hours while that from the permanganate oxidation for one hour only. A small quantity of sugar was formed during this acid hydrolysis, and a larger quantity if the time of heating was prolonged. A hydrazone resulted—possibly mannose-hydrazone. The alkaline hydrolysis need be continued for only ten to thirty minutes at a temperature of 70°–100°. For the new soluble oxycelluloses the name γ-oxycellulose has been proposed, it being considered entirely different to the class already distinguished by the prefix β.[1] The properties are briefly as follows:

The aqueous solution when dilute is opalescent or milky and yellow in transmitted light, is readily filterable, and does not alter on standing or when heated. More concentrated solutions (5%–10%) resemble glycerol or viscose, and when dried in a desiccator or over a water bath, both deposit silky transparent scales or plates. The addition of various metallic salts of acids or alcohol induces precipitation. When precipitated by an acid, the solubility greatly diminishes as the substance dries, but is restored by the action of warm sodium carbonate solution. If washed with almost any dilute acid the oxycellulose becomes insoluble once more and this cycle may be indefinitely repeated. Drying at 110°, however, does not permanently destroy the solubility. This γ-oxycellulose reduces Fehling's solution when heated, and forms a yellow hydrazone which is insoluble if prepared from the insoluble oxycellulose, but like it, becomes soluble by the action of alkali. Its solutions also become yellow and opalescent and deposit lustrous, golden colored scales. Iodine produces no coloration. The pentosan reaction does not take place, and the ash has an alkaline reaction.

γ-Oxycellulose in its soluble form would appear to be the sodium salt of a soluble acid which when dried becomes an insoluble anhydride or lactone.

According to A. Nastukoff,[2] the oxycellulose soluble in ammo-

[1] J. C. S. 1883, **43**, 22; Chem. News, 1882, **46**, 240; abst. J. S. C. I. 1884, **3**, 206, 291; Bull. Soc. Chim. 1883, **39**, 671; Chem. Ind. 1883, **6**, 353; Chem. Tech. Rep. 1883, **22**, II, 94; Dingl. Poly. 1883, **250**, 280; Jahr. Chem. 1883, **36**, 1366, 1777. Mon. prod. chim. 1883, 242.

[2] Ber. 1901, **34**, 3589; J. Russ. Phys. Chem. Soc. 1901, **33**, 678; J. Soc. Dyers Col. 1902, **18**, 16; abst. Chem. News, 1902, **86**, 306; J. S. C. I. 1902, **21**, 63.

nia which is obtained by boiling cellulose with nitric acid of 1.3 sp. gr., is termed β-oxycellulose, Cross and Bevan obtaining a yield of only 30% from cotton, the remainder being oxidized to oxalic acid.

O. v. Faber and B. Tollens[1] obtained a yield of 70%, and by the method of Nastukoff a yield of 90% is claimed. For the preparation of this β-oxycellulose the author takes a quantity of nitric acid of sp. gr. 1.3, equal only to 2.5 times the weight of the cellulose, and heats for one hour on the water bath. By this method a yield of 90% of oxycellulose which is completely soluble in boiling ammonia is obtained. Where larger proportions of acids are used, lower yields are said to result, correspondingly larger quantities of oxalic acid being produced. This author has also found that β-oxycellulose combines with barium to form a salt containing about 5% of barium. On the other hand γ-oxycellulose prepared with bleaching powder gives a barium salt containing only about one per cent. of barium. The various β-oxycelluloses and its salts are hard, while the γ-compounds are brittle. On evaporating solutions of sodium salts with γ-oxycellulose, lustrous films result which are easily detached from the glass whereas solutions of β-oxycellulose salts leave no such films. It is true, however, that by evaporation in a desiccator films are formed, but they are entirely different. The salts of β-oxycellulose decrease considerably in solubility after drying at 80° to

---

[1] Ber. 1899, **32**, 2589; abst. J. S. C. I. 1899, **28**, 1014; J. C. S. 1899, **76**, i, 854; Chem. Centr. 1899, **70**, II, 901; Jahr. Chem. 1899, **52**, 1292; Chem. Ztg. Rep. 1899, **23**, 321; Chem. Tech. Rep. 1899, **38**, 550; Bull. Soc. Chim. 1900, **24**, 621. B. Scholl (Ber. 1911, **44**, 1312; abst. J. C. S. 1911, **100**, i, 525; J. S. C. I. 1911, **30**, 739; Bull. Soc. Chim. 1911, **10**, 1644; Rep. Chim. 1911, **11**, 408; Chem. Zentr. 1911, **82**, II, 80; Chem. Ztg. Rep. 1911, **35**, 340; Kunst. 1911, **1**, 453), has devised the following simple experiment to demonstrate the reducing properties of cellulose. The specimen to be tested is digested for a few seconds with a dilute aqueous solution of flavanthrene (D. R. P. 136015, 138119, 139633, 139835, 140573, 141355, 142963. Scholl, Ber. 1903, **36**, 3436; 1907, **40**, 1692; 1910, **43**, 346; abst. J. C. S. 1904, **86**, i, 110; 1907, **92**, i, 540), dilute sodium hydroxide solution and solid sodium hyposulfite. After washing, the yellow dye is developed by exposing the fabric to the air for a few minutes, or by treatment with hypochlorite solution. By heating the fabric to boiling with 2*N* NaOH solution the blue color is restored. The length of time required for the reduction depends upon the amount of hydro-cellulose and oxycellulose present in the original specimen. Oxycelluloses give an immediate blue color, but when the oxycelluloses are removed by previous boiling with caustic soda solution, a longer time is required for the development of the blue color, and the alkaline extract produces the coloration more rapidly than does pure alkali. The pyranthrones or anthraquinoneazines may replace the flavanthrene.

110° whereas the solubility of the salts of γ-oxycellulose are not appreciably affected by this treatment.

R. Oertel[1] has prepared oxycellulose by treating cellulose in a neutral 15% solution of potassium chloride which was subsequently subjected to electrolysis. The cellulose is gradually attacked, being ultimately entirely transformed into soluble products. When from 60% to 70% of the cellulose has been dissolved, the residue of oxycellulose is found to be entirely soluble in cold 10% NaOH solution, while still further treatment yields an oxycellulose giving a stable colloid solution with water.

The "copper values" of the oxycellulose products as determined by C. Schwalbe's method[2] were unduly high, increasing with the degree of treatment, a maximum of 39.5 being recorded. The copper value was found not always to be in direct relationship with the solubility in sodium hydroxide. The furfural value of the oxycellulose prepared by electrolysis was 1.7%, the solubility of ordinary cotton being less than one per cent., while the furfural value is insufficiently definite to serve for the definite characterization of oxycellulose. When subjected to H. Ost's viscosity test,[3] oxycellulose showed the minimum value at an early stage. The susceptibility of oxycellulose to acid hydrolysis (Schwalbe's "hydrolysis-difference value") is high, being 12.12 as compared with 2.18 for normal cellulose.

When saccharified by 70% sulfuric acid according to the

1. Chem. Ztg. 1911, **35**, 713; abst. J. C. S. 1911, **100**, i, 607; J. S. C. I. 1911, **30**, 887; Chem. Zentr. 1911, **82**, II, 855. Zts. ang. Chem. 1913, **26**, I, 246; abst. C. A. 1913, **7**, 2302; J. C. S. 1913, **104**, i, 594; J. S. C. I. 1913, **32**, 595; Chem. Zentr. 1913, **84**, I, 2110; Chem. Ztg. Rep. 1913, **37**, 273; Kunst. 1913, **3**, 330; Wag. Jahr. 1913, **59**, II, 543.

2. Ber. 1907, **40**, 1347; Wochenbl. Papierfabr. **38**, 2535; abst. C. A. 1907, **1**, 1696, 2179; J. C. S. 1907, **92**, i, 390; J. S. C. I. 1907, **26**, 548; Bull. Soc. Chim. 1908, **4**, 1533; Rep. Chim. 1907, **7**, 318; Chem. Zentr. 1907, **78**, I, 1490; Chem. Ztg. Rep. 1907, **31**, 302; Jahr. Chem. 1905–1908, II, 961; Meyer Jahr. Chem. 1907, **17**, 215; Zts. ang. Chem. 1908, **21**, 265.

3. Ztg. ang. Chem. 1911, **24**, 1892; abst. C. A. 1912, **6**, 684; J. C. S. 1911, **100**, i, 838; J. S. C. I. 1911, **30**, 1247; Chem. Zentr. 1911, **82**, II, 1519; Chem. Ztg. Rep. 1911, **35**, 520; Meyer Jahr. Chem. 1911, **21**, 220; Wag. Jahr. 1911, **57**, II, 428. The method of oxycellulose estimation devised by G. Kita (J. Chem. Ind. Tokyo, 1917, **20**, 138; abst. J. S. C. I. 1917, **36**, 868; C. A. 1917, **11**, 2405) differs from Schwalbe's method in that it is not applicable to the determination of injury that may occur in the various treatments of cellulose as in bleaching. Compare E. Jandrier, Compt. rend. 1899, **128**, 1407; Bull. Soc. Chim. 1899, **21**, 895; abst. Chem. News, 1899, **80**, 11; J. C. S. 1899, **76**, i, 788; J. S. C. I. 1899, **18**, 711; Rev. Chim. 1899, **1**, 338; Chem. Centr. 1899, **70**, II, 184; Chem. Ztg. 1899, **23**, 517; Jahr. Chem. 1899, **52**, 1295.

method of H. Ost and L. Wilkening,[1] oxycellulose yields at the most only about 90% of the quantity of dextrose obtainable from cellulose. This would indicate that one in ten of the dextrose residues in the oxycellulose molecule is in the modified or oxidized condition. On acetylation, using zinc chloride as a catalyst and steeping the material for some days in glacial acetic acid prior to acetylation, oxycellulose was found to be much more readily esterified than cellulose, the product containing a greater proportion of acetone-soluble ester, and this portion was found to possess a lower laevo-rotatory power. On acetolysis according to Ost's method, oxycellulose yields only 20%–31% of crystallized cellobiose acetate[2] as compared with 40% from cellulose. Elementary analysis of oxycellulose as carried on by this author, showed C. 43.8% and H. 6.30%, from which is concluded that oxycellulose prepared by his process is an oxidized derivative of hydrolyzed cellulose and not a homogenous product, probably varying in the degree of modification in both directions. Hydrolytic modification of the cellulose in the production of the oxycellulose is indicated by the low viscosity of its solutions and the cupric-reducing power, the high proportion of acetate soluble in acetone and the low rotatory power of the normal acetic ester. The oxidized modification is indicated by an increased cupric-reducing power as compared with hydrocellulose, the low combined acetic acid in the acetic ester indicating suppression of hydroxyl groups, invariably accompanied by a low yield of dextrose on saccharification and a low yield of cellobiose on acetylation. W. Bancroft and R. Currie[3] have conducted experiments to ascertain to what extent the properties of oxycellulose or the oxycelluloses differ when prepared by the action of nitric acid, permanganate, chloric acid and bleaching powder on cellulose, and the results obtained afford no evidence for the

---

[1] Chem. Ztg. 1910, **34**, 461; abst. C. A. 1910, **4**, 1888; J. C. S. 1910, **98**, i, 365; J. S. C. I. 1910, **29**, 688; Bull. Soc. Chim. 1911, **10**, 61; Chem. Zentr. 1910, **81**, I, 2074; Jahr. Chem. 1910, **63**, II, 420; Meyer Jahr. Chem. 1910, **20**, 318; Wag. Jahr. 1910, **56**, II, 392; Ztg. ang. Chem. 1910, **23**, 1534. See E. Nölting and Rosenthal, Bull. soc. ind. Rouen, 1883, **10**, 170, 239. C. Kurz, Zts. Farb. Textilchem. 1902, **1**, 46; J. S. C. I. 1902, **21**, 405; Rep. Chim. 1902, **2**, 15; Chem. Centr. 1902, **73**, I, 956; Chem. Ztg. Rep. 1902, **26**, 79; Jahr. Chem. 1902, **55**, 1600; Wag. Jahr. 1902, **48**, II, 562.

[2] See Vol. 8 of this work.

[3] J. Phys. Chem. 1915, **19**, 159; abst. C. A. 1915, **9**, 964; J. C. S. 1915, **108**, i, 76; J. S. C. I. 1915, **34**, 274.

assumption of the existence of three different oxycelluloses. According to these authors the substance described as α-oxycellulose is apparently unchanged cellulose more or less contaminated with certain products of degradation. Except in regard to the degree of normal β- and γ-oxycellulose appear to be the same. None of the above oxidizing agents give a completely oxidized product, and it is doubtful therefore whether a pure oxycellulose has as yet been obtained. The reducing action on Fehling's solution is considered as not characteristic of oxycellulose, but more probably due to other products of the oxidation reaction. Experiments with a number of metallic mordants are recorded and indicate that these are not absorbed to any large extent.

A mixture of oxycellulose, made for example by treating cellulose with dilute nitric acid, and albuminous matter such as casein or glutin, may form into a plastic mass with the aid of ammonia.[1] The mass after being precipitated by means of acid is hardened, for example by means of formaldehyde, and then dried at 60°–80°. This composition is claimed to be advantageous in the manufacture of artificial silk.

R. Müller[2] has found in connection with a process for bleaching cotton and linen by immersion in an alkaline aqueous solution through which a current of air or oxygen is passed, that the presence of small quantities of other metal compounds, as, for instance, only 0.5% of cobalt oxide, causes the oxidation of fibrous materials to oxycellulose. The alkaline solutions mentioned as being especially suitable in this instance are the alkali hydrates, carbonates, chlorates and silicates. C. Kurz[3] proposes the use of oxycellulose in calico printing for the production of body colors in place of viscose. The oxycellulose is prepared by treating cotton with alkaline permanganate, the product thus obtained being allowed to stand in contact with fairly strong caustic soda for several

---

[1] Naamlooze Venootschap Hollandsche Zijde Maatschappij, E. P. 4521, 1913; abst. C. A. 1914, **8**, 2497; Kunst. 1914, **4**, 194. Gross and Bouchary (F. P. 487070, 1912) have described a process for the manufacture of oxalic acid and oxycellulose.

[2] E. P. 9369, 1910; abst. J. S. C. I. 1911, **30**, 82; see also F. P. 414821, 1910; abst. J. S. C. I. 1910, **29**, 1200.

[3] Zts. Farb. Textilchem. 1902, **1**, 46; J. Soc. Dyers Col. 1902, **18**, 143; abst. J. S. C. I. 1902, **21**, 405; Rep. Chim. 1902, **2**, 15; Chem. Centr. 1902, **73**, I, 956; Chem. Ztg. Rep. 1902, **26**, 79; Jahr. Chem. 1902, **55**, 1600; Wag. Jahr. 1902, **48**, II, 562; Rev. gen. mat. Col. 1901.

days, after which it is diluted with water and the oxycellulose precipitated by the addition of mineral acid and washed.

For printing, the oxycellulose paste is thickened with albumin and gum tragacanth, printed on and steamed. Zinc chloride may also be added to the printing color.

In the process for removing stains from textile fabrics caused by-oxycellulose, the Bleachers Association Limited and A. Benjamin and R. Hübner,[1] boil the textile fabrics for twenty minutes in a solution prepared by mixing 20 liters of a halogen containing about 17% of titanous chloride with one thousand liters of water. The material is then washed and if desired, soured with hydrochloric acid after which it is again washed. Upon dyeing fabrics thus treated with, for example, direct cotton dyestuffs, even dyeings are obtained while spots on parts which before the treatment with the titanous salt, were "tender" owing to the presence of oxycellulose in them, are, it is stated, very much stronger. Instead of titanous chloride, other titanous salts may be employed but this is the only one at present commercially available.

It has pointed out[2] that in one case at least the increased affinity which oxycellulose usually shows for basic coloring matters such as methylene blue, does not necessarily furnish a conclusive proof of its presence. More reliable results, in his estimation, are obtained by utilizing the property of oxycellulose to reduce Fehling's solution. For this purpose the material to be tested is first treated in such manner as to remove the substances used in finishing and then digesting on the water bath for fifteen minutes with a ten per cent. Fehling's solution and well rinsed with water. When oxycellulose is present the fiber is stated to be colored red.

W. Harrison[3] has reviewed the work of G. Witz,[4] A. Nastukoff,[5]

---

[1] E. P. 17653, 1902; abst. J. S. C. I. 1902, **31**, 1328; Chem. Ztg. 1903, **27**, 1259.

[2] Zts. öffentl. Chem. 1909, 524; abst. J. Soc. Dyers Col. 1910, **17**, 69.

[3] J. Soc. Dyers Col. 1912, **28**, 359; abst. J. S. C. I. 1913, **32**, 17; Meyer Jahr. Chem. 1912, **22**, 508. A process for the manufacture of salts-free oxycellulose, has been described by R. Adler in D. R. Anm. A-25211; Chem. Zentr. 1919, II, 387.

[4] Bull. soc. ind. Rouen, 1883, **11**, 188; abst. J. S. C. I. 1883, **2**, 378; Mon. Sci. 1883, **25**, 517; 1884, **26**, 116; Dingl. Poly. 1883, **250**, 271; Jahr. Chem. 1883, **36**, 1782; Wag. Jahr. 1883, **29**, 1068. Färb. Must. Ztg. **17**, 129; Tech. Chem. Jahr. 1884–1885, 473.

[5] J. Russ. Phys. Chem. Soc. 1900, **32**, 543; 1901, **33**, 310, 678; Ber. 1900, **33**, 2239;1901, **34**, 719, 3589; abst. Chem. News, 1902, **86**, 306; J. C. S.

E. Berl and R. Klaye,[1] and O. von Faber and B. Tollens,[2] and concludes that none of the tests described by them, nor those of Vetillart[3] and H. Ditz,[4] are capable of distinguishing between oxycellulose and hydrocellulose. He asserts that the evidence available apparently indicates that the different forms of oxycellulose and hydrocellulose are absorption compounds of peptized cellulose and the products of hydrolysis of cellulose. The dyeing properties, therefore, depend mainly upon the colloidal state of the cellulose portion, the reducing properties being due to the products of hydrolysis. If this is so, it therefore would appear probable that the absorbed reducing substances are of an aldehydic nature in hydrocellulose and of an acidic nature in oxycellulose. For the detection of reducing substances (oxycellulose or hydrocellulose) in fabrics, the author recommends a reagent prepared by adding silver nitrate to sodium thiosulfate solution with vigorous stirring, and then adding sodium hydroxide so as to obtain a liquid containing silver nitrate one per cent. sodium thiosulfate four per cent. and sodium hydroxide four per cent. If the material be boiled in this solution and then steamed, the portions containing oxycellulose or hydrocellulose are stained. The effect is said to be enhanced if the material be heated with a one per cent. solution of phenylhydrazine in glacial acetic acid and then washed thoroughly with dilute acetic acid before treating

---

1900, **78**, i, 540; J. S. C. I. 1900, **19**, 733; 1901, **20**, 63, 573; J. Soc. Dyers Col. 1901, **17**, 122; Bull. Soc. Chim. 1901, **26**, 123, 557; 1902, **28**, 130, 481; Rep. Chim. 1901, **1**, 414; 1902, **2**, 189; Chem. Centr. 1900, **71**, II, 430; 1901, **72**, I, 99, 932; II, 335, 1263; Chem. Ztg. Rep. 1900, **24**, 258; 1901, **25**, 122, 353; Jahr. Chem. 1900, **53**, 844; 1901, **54**, 897, 898; Meyer Jahr. Chem. 1901, **11**, 441; Zts. ang. Chem. 1900, **13**, 1083.

[1] Zts. Schiess-Spreng. 1907, **2**, 381, 403; abst. C. A. 1908, **2**, 184; J. C. S. 1908, **94**, i, 504; J. S. C. I. 1907, **26**, 1157; Chem. Zentr. 1908, **79**, I, 1381; Chem. Ztg. Rep. 1908, **32**, 43; Jahr. Chem. 1905–1908, II, 976.

[2] Ber. 1899, **32**, 2589; abst. J. S. C. I. 1899, **28**, 1014; J. C. S. 1899, **76**, i, 854; Chem. Centr. 1899, **70**, II, 901; Jahr. Chem. 1899, **52**, 1292; Chem. Ztg. Rep. 1899, **23**, 321; Chem. Tech. Rep. 1899, **38**, 550; Bull. Soc. Chim. 1900, **24**, 621.

[3] Bull. soc. ind. Rouen, 1883, **11**, 234, 934.

[4] Chem. Ztg. 1907, **31**, 833, 844, 857; abst. C. A. 1907, **1**, 2941; J. C. S. 1907, **92**, i, 129; J. S. C. I. 1907, **26**, 988, 1026; Bull. Soc. Chim. 1907, (4), **2**, 1468; Chem. Zentr. 1907, **78**, II, 1606; Jahr. Chem. 1905–1908, II, 964; Meyer Jahr. Chem. 1907, **17**, 504; Zts. ang. Chem. 1908, **21**, 1185; reproduced J. prakt. Chem. 1908, (2), **78**, 343. In this connection see also L. Meyer, Chem. Ztg. 1907, **31**, 902; abst. C. A. 1908, **2**, 180; Chem. Zentr. 1907, **78**, II, 1607; Jahr. Chem. 1905–1908, II, 964. C. Councler, Zts. Forst. u. Jagdwesen, **27**, 427. L. Meyer, Zts. Forst. u. Jagdwesen, **29**, 428.

with the silver solution, but excess of the latter must be avoided.

In conjunction with the observations of Harrison, it is maintained by L. Lloyd[1] that the reaction of Ditz is entirely reliable when carried out as follows: The cotton is boiled with water, about one-fifth the volume of Fehling's solution is added and the vessel suspended for about half an hour in boiling water; the cotton is then removed from the solution and well washed with water. With material which gives by tensile strength tests a five per cent. tendering, a faint pink deposit is observable on the material. Increase in the amount of oxycellulose will in some cases also result in the precipitation of cuprous oxide in the liquid. By applying the reaction as above given the author claims to be able to prove the formation of oxycellulose by the action of ammonia and metallic salts upon cotton in a moist atmosphere at 50°.

A. Knaggs[2] in working upon the test as devised by E. Knecht[3] to determine whether cotton has been mercerized or not and obtained by dyeing the sample in a weak solution of benzopurpurin, found that upon carefully reducing with titanous chloride, the shade on mercerized material appears bluish red just before the dyestuff is all destroyed, whereas upon unmercerized cotton the color is bluish violet. In some cases this reduction is found unnecessary for when strong hydrochloric acid is added drop by drop to the dilute dye-bath in which the samples of mercerized and unmercerized cotton are lying, the shade of the unmercerized piece becomes blue at the time when the mercerized sample appears a bright red color.

This difference is not attributable to alkali remaining in the mercerized material for this may be treated with acid until the shade becomes blue and then returned to the dye-bath when the red shade will reappear. In respect to oxycellulose it has been found that when for instance a piece of cotton spotted with bleaching powder or other agent capable of producing oxycellulose is rinsed in acid and finally with water it will be dyed a deep shade with benzopurpurin. However, upon placing in the acid so

---

[1] J. Soc. Dyers Col. 1910, **26**, 273; abst. C. A. 1911, **5**, 1843; J. S. C. I. 1910, **29**, 1450; Meyer Jahr. Chem. 1910, **20**, 487.

[2] J. Soc. Dyers Col. 1908, **24**, 112; abst. J. S. C. I. 1908, **27**, 442; Chem. Ztg. Rep. 1908, **32**, 315.

[3] J. Soc. Dyers Col. 1908, **24**, 67, 68; abst. J. S. C. I. 1908, **27**, 400; Chem. Ztg. Rep. 1908, **32**, 272; Wag. Jahr. 1908, **54**, II, 467.

that the shade becomes blue and then rinsing in water until the red color on the ordinary cotton reappears, those parts which have been converted into oxycellulose are said to remain a blue-black in color.

According to G. Kita,[1] the method of estimating oxycellulose suggested by H. Nishida[2] and consisting in treating with a known quantity of methylene blue solution and then titrating the excess of dyestuff not fixed by the oxycellulose with titanium chloride is untrustworthy, because the quantity of dyestuff fixed is influenced by the degree of saponification of the substance under examination and by other factors, and furthermore there is no proportionality between the color of the oxycellulose and the amount of methylene blue absorbed. Though it may be conveniently used in certain special instances, this method is not considered applicable in the same broad way, as Schwalbe's copper value for the determination of the damage caused by various treatments of cellulose.

M. Saget[3] has called attention to the fact that the diminution in strength which occurs in cream-tinted linen on bleaching, depends to a large extent upon the method used for cream-tinting, and is due primarily to the formation of oxycellulose during the latter process. This oxycellulose, however, cannot be detected in a chemical manner as the linen itself is yellow and contains impurities, but may be determined by measuring the strength of the fiber on steaming and on treatment in an alkaline bath. The presence or absence of chlorine in a fiber is not of necessity indicative of the strength of the material. Linen which has been partially converted into oxycellulose tenders under the influence of rain and sunlight.

Acetolysis and Octa-Acetylcellobiose. Decomposition of cellulose to cellobiose first caused by Skraup and his pupils by means of acetic acid anhydride in the presence of sulfuric acid is the process called acetolysis, and is of especial importance in this connection because as a result of the investigations in this direction,

---

[1] J. Chem. Ind. Tokyo, 1917, **20**, 138, 219; abst. J. S. C. I. 1917, **26**, 868; C. A. 1917, **11**, 2405.

[2] Kunst. 1914, **4**, 266; abst. C. A. 1914, **8**, 3236; Zts. ang. Chem. 1914, **27**, II, 605.

[3] J. Soc. Dyers Col. 1914, **30**, 331; abst. C. A. 1915, **9**, 1394; J. S. C. I. 1914, **33**, 1151; Zts. ang. Chem. 1915, **28**, I, 71.

much has been revealed as to the mechanism of the process of acetylation and hydrolysis.

Z. Skraup,[1] in repeating the work of Franchimont, found that when cellulose is treated with sulfuric acid and acetic acid anhydride, if low temperatures and small quantities of sulfuric acid are used, the products are more complicated than when these precautions are not observed.

What was at first considered to be a pentacetylhexose was afterwards[2] shown to be a cellobiose octacetate, of crystalline structure, and melting at 227°–228°, and yielding upon saponification a biose, cellobiose. By the action of hydrochloric acid on the acetyl derivative, an acetochloro compound results, from which, by replacing the chlorine by acetyl, a new acetyl compound was obtained of m. pt. 200°, isomeric with the product mentioned above. A heptaacetylchlorocellobiose, formed by the action of HCl on heptacetylcellobiose, melted at 178°.[3]

[1] Ber. 1899, **32**, 2413; abst. J. C. S. 1899, **76**, 852; Jahr. Chem. 1899, 1288; J. S. C. I. 1899, **18**, 941; Chem. Centr. 1899, **70**, II, 752; Bull. Soc. Chim. 1900, (3), **24**, 619. W. Hoffmeister, Landw. Versuchstat, 1891, **39**, 461; abst. J. S. C. I. 1892, **11**, 452; J. C. S. 1892, **62**, 129; Ber. 1893, **26**, R, 497; Chem. Centr. 1892, **63**, I, 27; Chem. Ztg. Rep. 1891, **15**, 317; Jahr. Chem. 1891, **44**. 2180; Wag. Jahr. 1891, **37**, 1105; Zts. ang. Chem. 1891, **4**, 709.

M. Hoenig and S. Schubert, Monatsh. Chem. 1885, **6**, 708; 1886, **7**, 455; abst. J. C. S. 1886, **50**, 44; 1887, **52**, 125; Bull. Soc. Chim. 1886, **46**, 517; 1887, **47**, 578; Ber. 1885, **18**, R, 614; 1886, **19**, R, 748; Chem. Tech. Rep. 1886, **25**, II, 218; Jahr. Chem. 1885, **38**, 1575, 1576, 1577; 1886, **39**, 1780; Wag. Jahr. 1886, **32**, 610.

[2] Z. Skraup and J. Koenig, Ber. 1901, **34**, 1115; J. S. C. I. 1901, **20**, 740; J. C. S. 1901, **80**, i, 370; Jahr. Chem. 1901, 878; Chem. Centr. 1901, I, 1197; J. Soc. Dyers Col. 1901, **16**, 85, 203.

[3] Z. Skraup and J. Koenig, Monatsh. 1901, **22**, 1011; abst. Centr. 1902, **75**, 183; J. S. C. I. 1902, **21**, 144. Compare K. Kellermann and I. McBeth, Centr. Bakt. 1912, **34**, II, 485; Chem. Zentr. 1912, **83**, II, 856; C. A. 1912, **6**, 1763. H. Pringsheim, Zts. physiol. Chem. 1912, **78**, 266; abst. C. A. 1912, **6**, 2632; J. C. S. 1912, **102**, ii, 587; J. S. C. I. 1912, **31**, 531; Bull. Soc. Chim. 1913, **14**, 398; Chem. Zentr. 1912, **83**, II, 538; Meyer Jahr. Chem. 1912, **22**, 254. For acetochlorglucose and acetochlorgalactose, see Z. Skraup and R. Kremann, J. C. S. 1902, **82**, i, 135; Monatsh. Chem. 1901, **22**, 1037; abst. J. S. C. I. 1902, **21**, 144; Bull. Soc. Chim. 1902, (3), **28**, 928; Monatsh. 1902, **22**, 375; abst. Bull. Soc. Chim. 1902, (3), **28**, 482; J. S. C. I. 1901, **20**, 513. For other carbohydrate acetates, see β-acetobromgalactose, alphaglucosepentacetate, E. Fischer and E. Armstrong, Ber. 1901, **34**, 2885; 1902, **35**, 833, 3153; abst. Sitzungsber. Akad. Wiss. Ber. 1901, **7**, 123; J. S. C. I. 1901, **20**, 1151; 1902, **21**, 1302; J. C. S. 1901, **78**, i, 189; 1902, **80**, i, 746; Chem. Centr. 1901, I, 679; II, 981; 1902, I, 758; Jahr. Chem. 1901, 847; 1902, 1005; Bull. Soc. Chim. 1902, (3), **28**, 128, 524; 1903, (3), **30**, 591; Rep. Chim. 1902, **2**, 241. α-Acetochlorlactose, β-heptacetobrommaltose, E. Fischer and E. Armstrong, Ber. 1902, **35**, 841, 3153. Heptacetochlormaltose, E. Fischer and E. Armstrong, Ber. 1901, **34**, 2895; 1902, **35**, 840, 3153. β-Methylmaltosideheptacetate, E. Fischer and E. Armstrong, Ber. 1901, **34**,

A large number of these interesting derivatives have been prepared,

---

2895. β-Phenolmaltoside, E. Fischer and E. Armstrong, Ber. 1902, **35**, 3153. β-Phenolmaltosideheptacetate, E. Fischer and E. Armstrong, Ber. 1902, **35**, 3153. β-Acetobromglucose, W. Koenigs and E. Knorr, Ber. 1901, **34**, 962; abst. J. S. C. I. 1902, **21**, 196; J. C. S. 1902, **82**, i, 135; Chem. Centr. 1902, I, 302; Rept. Chimie, 1901, **1**, 470; Bull. Soc. Chim. 1902, (2), **28**, 317. β-Acetochlorglucose, A. Colley, Compt. rend. 1870, **70**, 401; **71**, 436; abst. J. C. S. 1873, **26**, 1612; Jahr. Chem. 1870, 841; Ber. 1870, **3**, 212; 1871, **4**, 933; Bull. Soc. Chim. 1870, **14**, 58; 1873, **19**, 406. β-Acetochlorlactose, Z. Skraup and R. Kremann, Monatsh. Chem. 1901, **22**, 375; abst. J. S. C. I. 1901, **20**, 513; J. C. S. 1901, **80**, i, 506; Zeit. ang. Chem. 1901, **14**, 371; Chem. Centr. 1901, II, 194; Bull. Soc. Chim. 1902, (3), **28**, 482; Rept. Chimie, 1901, **1**, 438; Jahr. Chem. 1901, 846. α-Acetonitroglucose, A. Colley, Compt. rend. 1873, **76**, 436; abst. J. C. S. 1873, **27**, 612; Bull. Soc. Chim. 1873, (2), **19**, 406; Ber. 1873, **6**, 197; Jahr. rein. Chem. 1873, **1**, 114. Arabic acid-nitrile-tetracetate, A. Wohl, Ber. 1893, **26**, 732; See also Ber. 1891, **24**, 993; Jahr. Chem. 1891, 2171; abst. J. C. S. 1893, **64**, i, 292; Wag: Jahr. 1893, **39**, 867; Bull. Soc. Chim. 1893, **10**, 792; Minuni Jahr. organ. Chem. 1893, 251; Jahr. Chem. 1893, 859. Arabinose tetracetate, xylose tetracetate, W. Stone, Am. Chem. J. 1893, **15**, 653; abst. Jahr. Chem. 1893, 852; Ber. 1894, **27**, R, 83; Jahr. organ. Chem. 1893, **1**, 251, 253. Cellose-β-octacetate, L. Maquenne and W. Goodwin, Bull. Soc. Chim. 1904, (3), **31**, 854; abst. J. C. S. 1904, **86**, i, 799; Chem. Centr. 1904, II, 644; Jahr. Chem. 1904, 1149; Rept. de Chim. 1905, **5**, 55; Rev. Sci. 1904, (5), **2**, 181; Rev. gén. sci. 1904, **15**, 668. Erythrite tetracetate, G. Griner, Bull. Soc. Chim. 1893, (3), **9**, 218; Compt. rend. 1893, **116**, 723; **117**, 553; abst. J. C. S. 1893, **64**, i, 450; Jahr. Chem. 1893, 660; Jahr. organ. Chem. 1893, **1**, 27; Ber. 1893, **26**, 314, 773, 931; Mon. Sci. 1893, 952; Chem. News, **67**, 193, 289; Jahr. Chem. 1893, **3**, 130. α-Ethylmaltosideheptacetate, Foerg, Monatsh. Chem. 1902, **23**, 44; Wien. Acad. Ber. **110**, IIB, 1054; abst. J. S. C. I. 1902, **21**, 506; J. C. S. 1902, **82**, i, 347; Zeit. ang. Chem. 1902, **14**, 1210; Chem. Centr. 1902, I, 861; Jahr. Chem. 1901, 877; Rept. Chim. 1902, **2**, 203; Bull. Soc. Chim. 1903, (3), **30**, 335. *d*-Fructose-pentacetate, E. Erwig and W. Koenigs, Ber. 1890, **23**, 672; abst. J. C. S. 1890, **58**, 732; Bull. Soc. Chim. 1890, (3), **3**, 12; Δ-Fructose-tetracetate, F. Jaeger, Zts. Kryst. 1908, **45**, 539; abst. J. C. S. 1908, **94**, i, 413; C. A. 1908, **2**, 2076; Rep. de Chimie, 1908, 266, 417; Bull. Soc. Chim. 1909, (4), **6**, 326. Galactonic acid lactone-chlorhydrin-triacetate, O. Ruff and A. Franz, Ber. 1902, **35**, 943; abst. Chem. Zentr. 1902, I, 858; Jahr. Chem. 1902, 888; Rept. de Chim. 1902, **2**, 372; Bull. Soc. Chim. 1902, (3), **28**, 524. Galactonic acid-nitrile-pentacetate, A. Wohl and E. List, Ber. 1897, **30**, 3101; abst. J. S. C. I. 1898, **17**, 170; J. C. S. 1898, i, 168; Chem. Centr. 1898, I, 372; Bull. Soc. Chim. 1898, **20**, 289. β-Galactose-pentacetate, E. Erwig and W. Koenigs, Ber. 1889, **22**, 2207; 1890, **23**, 672; abst. J. S. C. I. 1889, **8**, 718, 994; 1890, **9**, 637; J. C. S. 1889, **56**, 952, 991, 1131; 1890, **58**, 732; Chem. Centr. 1889, **60**, 748; Jahr. Chem. 1889, 1692, 2041; 1890, 2132; Bull. Soc. Chim. 1890, (3), **3**, 12, 24; **4**, 517, 557. Gluconic acid ethyl ester-pentacetate, F. Volpert, Ber. 1886, **19**, 2621; abst. J. C. S. 1887, **52**, 127; Jahr. Chem. 1886, 1379; Chem. Ind. 1886, 351; Bull. Soc. Chim. 1887, (2), **47**, 775. Gluconic acid lactone-tetracetate, tetracetyl-*d*-gluconolactone), C. Paal and F. Hoernstein, Ber. 1906, **39**, 1361; abst. J. C. S. 1906, **90**, i, 400, 802; Chem. Centr. 1906, II, 1182; Bull. Soc. Chim. 1907, (4), **2**, 1281. Glucose diacetate and triacetate, S. Acree and J. Hinkins, Am. Chem. J. 1902, **28**, 370; abst. J. C. S. 1903, **84**, i, 218; Chem. Centr. 1903, I, 76; Jahr. Chem. 1902, 1013; J. A. C. S. 1903, **25**, R, 78, 130; Bull. Soc. Chim. 1904, (3), **32**, 191. Glucose tetracetate, C. Istrati and L. Edeleanu, Chem. Ztg. Rep. 1892, **16**, 102; abst. Bull. Soc. Sci. Fiz. Bucuresci, **1**, 46; J. C. S. 1892, **62**, 1293; Chem. Centr. 1892, I, 624; Jahr. Chem. 1892, 2448. Glucose tetracetate, D. Law, Chem. Ztg. 1908, **32**, 365; abst. J. C. S. 1908, **94**, 321; Zeit. ang. Chem. 1908, **21**, 1317; Chem.

and their reactions and physical constants carefully investigated.

Zentr. 1908, I, 1831; Bull. Soc. Chim. 1909, (4), **6**, 157. Glucoseamin-triacetate-bromhydrin, M. Hamlin, J. A. C. S. 1911, **33**, 766; abst. C. A. 1911, **5**, 2643; J. C. S. 1911, **100**, i, 529; Chem. Zentr. 1911, II, 443; Rept. Chimie 1911, II, 374; Chem. Ztg. Rep. 1911, **35**, 369; Bull. Soc. Chim. 1912, (4), **12**, 83. β-Glycose pentacetate, A. Franchimont, Ber. 1879, **12**, 1938; Compt. rend. 1879, **89**, 711; abst. J. C. S. 1880, **38**, 158; Jahr. Chem. 1879, 832; Jahr. rein Chim. 1879, **7**, 501; Mon. Sci. 1879, 1250; Chem. News, 1879, **40**, 264. Glycuronic acid lactone-bromhydrindiacetate (diacetylbromoglycuronic lactone), C. Neuberf and W. Neimann, Zts. physiol. Chem. 1905, **44**, 114; abst. J. C. S. 1905, **88**, i, 412; Chem. Centr. 1905, I, 1086; Bull. Soc. Chim. 1905, **34**, (4), 993. Inosite hexabenzoate, L. Maquenne, Bull. Soc. Chim. 1887, **48**, (2), 54; Compt. rend. 1887, **104**, 1719; abst. J. C. S. 1887, 355, 459, 908; Chem. Ind. 1887, **10**, 443; Ber. 1887, **20**, 478, 696; Mon. Sci. 1887, 871; Chem. News, 1887, **56**, 23, 279. Inosite hexacetate, C. Tanret, Bull. Soc. Chim. 1895 (3), **13**, 261; Compt. rend. 1895, **120**, 228; abst. Jahr. Chem. 1895, 1303; J. Pharm. Chim. (6), **1**, 228; Mon. Sci. 1895, **44**, 306; Rev. gén. sci. 1895, **6**, 438. Inosite pentacetate, H. Müller, J. C. S. 1907, **91**, 1780; abst. C. A. 1908, **2**, 796, 1001; J. S. C. I. 1907, **26**, 1293; Chem. Zentr. 1908, I, 268; Bull. Soc. Chim. 1908, (4), **4**, 904; Chem. News, 1907, **96**, 243; Rept. de Chim. 1908, **8**, 177. Isomeric lactose octoacetates, C. Hudson and J. Johnson, J. A. C. S. 1915, **37**, 1270; abst. Chem. Zentr. 1915, II, 321. Lactose mono- and di-acetate, Demole, Ber. 1879, **12**, 1935; Bull. Soc. Chim. 1879, (2), **32**, 489; abst. Arch. phys. Nat. (3), **2**, 408; Jahr. Chem. 1879, 857; J. C. S. 1880, **38**, 29; Jahr. rein Chem. 1879, **7**, 498; Chem. News, 1879, **40**, 156; 1880, **41**, 48. Lactose octoacetate, A. Herzfeld, Ber. 1880, **13**, 265; abst. J. C. S. 1880, **38**, 619; Chem. Centr. 1890, 757; Jahr. Chem. 1880, 1011; 1882, 880; Bull. Soc. Chim. 1181, (2), **35**, 250. Levosine acetate, C. Tanret, Bull. Soc. Chim. 1891, (3), **5**, 724; Compt. rend. 1891, **112**, 293; abst. J. S. C. I. 1891, **10**, 473; J. C. S. 1891, **60**, 661; Jahr. Chem. 1891, 2177; Tech. Chem. Jahrb. 1891, **14**, 273; Mon. Sci. 1891, 312; Chem. News, 1891, **63**, 119; 1891, **64**, 61; Rev. gén. sci. 1891, **2**, 91. Lichenine triacetate, Husemann and Hilger, Die Pflanzenstoffe, 2d Ed. 129. Maltose octoacetate, A. Herzfeld, Ann. 1883, **220**, 215; Ber. 1895, **28**, 440; abst. J. S. C. I. 1883, **2**, 482; J. C. S. 1883, **43**, 652; Jahr. Chem. 1883, 1099, 1363; Wag. Jahr. 1883, 679; Ber. 1883, R, 2672; Bull. Soc. Chim. 1884, (2), **42**, 34, 533. Maltose-monoacetate, H. Yoshida, Ber. 1881, **14**, 365; abst. J. C. S. 1881, **40**, 568; Jahr. Chem. 1881, 984; Chem. News, 1881, **43**, 29. Mannite hexacetate, Franchimont, Ber. 1879, **12**, 2059; abst. J. C. S. 1880, **38**, 104; Jahr. Chem. 1879, 598; Jahr. rein Chem. 1879, **7**, 503; Bull. Soc. Chim. 1880, (2), **34**, 354. Melibiose octacetate, C. Scheibler and H. Mittelmeier, Ber. 1890, **23**, 1438; see also Ber. 1889, **22**, 1678, 3118; abst. J. S. C. I. 1889, **8**, 718; 1890, **9**, 311, 815; J. C. S. 1889, **56**, 953; 1890, **58**, 226, 1085; Jahr. Chem. 1889, 2058; 1890, 2146; Bull. Soc. Chim. 1890, **4**, 513, 515; 1891, **5**, 714; Wag. Jahr. 1889, **35**, 943; 1890, **36**, 945. β-Methylglucose-tetracetate, Koenigs and Knorr, Ber. 1901, **34**, 966; abst. J. S. C. I. 1902, **21**, 196; J. C. S. 1902, **82**, i, 135; Chem. Centr. 1902, I, 302; Bull. Soc. Chim. 1902, (2), **28**, 317; Rept. Chimie, 1901, **1**, 470. Mucic acid tetracetate, L. Maquenne, Bull. Soc. Chim. 1887, **48**, (2), 719; abst. J. C. S. 1888, **54**, 676; Jahr. Chem. 1887, 1777; Ber. 1888, **21**, R, 186; Chem. News, 1888, **57**, 161. Quercite acetate, F. Homann, Ann. 1878, **190**, 282; see also Ber. 1875, **8**, 1039; abst. J. C. S. 1878, **34**, 399; Jahr. Chem. 1877, 535; 1875, 799; Ber. 1875, **8**, 1039; 1879, **11**, 252; Bull. Soc. Chim. 1876, (2), **25**, 302. *o*-Quinitediacetate, L. Brunel, Bull. Soc. Chim. 1903, (3), **29**, 131, 231; Compt. rend. 1902, **135**, 1055; 1903, **136**, 383; abst. J. C. S. 1903, **84**, i, 157, 338; Chem. Centr. 1903, I, 233, 583, 711, 970; Jahr. Chem. 1902, 1344; 1903, 1116; Chem. News, **87**, 16; **88**, 70; Rept. de Chim. 1903, **3**, 129, 227, 205, 277. Saccharic acid-ethylester-tetracetate, A. Baltzer, Ann. 1869, **149**, 237; see also Naturf. Ges.

L. Maquenne and W. Goodwin,[1] preparing cellobiose by a

Zürich, 1867, 303; Zts. Chem. **4,** 219; abst. Jahr. Chem. 1868, 544; Bull. Soc. Chim. 1868, (2), **10,** 263. Scillite hexacetate, J. Mueller, Ber. 1907, **40,** 1821; abst. C. A. 1907, **1,** 2109; J. C. S. 1907, **92,** i, 482; Chem. Zentr. 1907, II, 51; Rept. de Chim. 1907, **7,** 364; Bull. Soc. Chim. 1908, (4), **4,** 1509. Sorbite hexacetate, C. Vincent and B. Delachanal, Compt. rend. 1889, **109,** 676; abst. J. S. C. I. 1890, **9,** 311; J. C. S. 1890, **58,** 21; Jahr. Chem. 1889, 1352; Ber. 1891, **23,** 24; Chem. News, 1889, **59,** 120; **60,** 258. Sucrose octoacetate, A. Herzfeld, Ber. 1880, **13,** 267; abst. J. C. S. 1880, **38,** 619; Chem. Centr. 1890, 757; Jahr. Chem. 1880, 1011; 1882, 880; Bull. Soc. Chim. 1881, (2), **35,** 250. Xylan monoacetate, R. Bader, Chem. Ztg. 1895, **19,** 55; abst. J. C. S. 1896, **70,** i, 335; Jahr. Chem. 1895, 1297; Ber. 1895, **28,** 427. Xylite pentacetate, G. Bertrand, Bull. Soc. Chim. 1891, (3), **5,** 556, 740; abst. J. S. C. I. 1891, **10,** 716; J. C. S. 1892, **62,** 28, 29; Ber. 1891, **24,** R, 530, 567. Heptacetobromlactose, menthol-maltoside, menthol-maltoside-heptacetate, E. and H. Fischer, Ber. 1910, **43,** 2530; abst. C. A. 1910, **4,** 3234; J. C. S. 1910, **98,** A, i, 716; Chem. Zentr. 1910, II, 1456; Rept. Chimie, 1911, **11,** 108; Chem. Ztg. Rep. 1910, 534; Bull. Soc. Chim. 1911, (4), **10,** 702. Manneo-tetrose-tetradekacetate, mannino-triose-hendekacetate, C. Tanret, Bull. Soc. Chim. 1902, **27,** (3), 947; Compt. rend. 1902, **134,** 1586; abst. J. S. C. I. 1902, **21,** 1033; J. C. S. 1902, **82,** i, 661; Chem. Centr. 1902, II, 347, 1177; Rev. gén. sci. 1902, **13,** 701; Jahr. Chem. 1902, 1031; Mon. Sci. 1902, (4), **14,** 621; Chem. News, 1903, **87,** 142; Rev. Sci. 1902, (4), **18,** 52. β-Glucose pentacetate, lactose tetracetate, glucose di- and triacetate, Schuetzenberger and Naudin, Bull. Soc. Chim. 1869, (2), **12,** 204; abst. J. C. S. 1872, **25,** 366; Chem. Centr. 1869, 681; 1871, 740; Jahr. Chem. 1869, 750; Zts. Chem. 1869, 264; Ber. 1869, 163, 556. Mannite acetate, P. Schuetzenberger, Ann. Chim. Phys. 1870, (4), **21,** 256. Glycogen triacetate, P. Schuetzenberger, Ann. 1871, **160,** 80; Ann. Chim. Phys. 1870, (4), **21,** 235; abst. J. C. S. 1872, **25,** 366; Chem. Centr. 1871, 740. Sucrose acetate, Schuetzenberger and Naudin, Compt. rend. 1869, **68,** 814; abst. Bull. Soc. Chim. 1869, (2), **12,** 107, 204, 206; 1868, (2), **10,** 128; reproduced in Ann. 1871, **160,** 80; Chem. Centr. 1869, 681; Jahr. Chem. 1869, 750; Zts. Chem. 1869, 264; Ber. 1869, 163, 556.

[1] Bull. Soc. Chim. 1904, (3), **31,** 854; abst. J. C. S. 1904, **86,** i, 799; Chem. Centr. 1904, II, 645; Jahr. Chem. 1904, I, 1149. According to H. Fenton and M. Gostling, various forms (J. C. S. 1898, **73,** 554; 1899, **75,** 423; 1901, **79,** 361, 807; abst. Chem. News, 1898, **77,** 282; 1899, **79,** 124; 1901, **83,** 92, 272; J. S. C. I. 1899, **18,** 404; Bull. Soc. Chim. 1899, **22,** 782; 1901, **26,** 341, 796; Rep. Chim. 1901, **1,** 424; Chem. Centr. 1898, **69,** II, 181, 421; 1899, **70,** I, 877, 1162; 1901, **72,** I, 679, 775; II, 123, 426; Chem. Ztg. 1898, **22,** 493; 1899, **23,** 225; 1901, **25,** 108, 507; Jahr. Chem. 1898, **51,** 1312; 1899, **52,** 2176; 1900, **53,** 1442; 1901, **54,** 838, 1494; Meyer Jahr. Chem. 1898, **8,** 202; 1899, **9,** 181; 1901, **11,** 223; Zts. ang. Chem. 1901, **14,** 273) and H. Fenton (Proc. Chem. Soc. 1901, **17,** 166; abst. Chem. News, 1901, **84,** 7; J. S. C. I. 1901, **20,** 757; Rep. Chim. 1901, **1,** 515; Chem. Centr. 1901, **72,** II, 405; Chem. Ztg. 1901, **25,** 591; Jahr. Chem. 1901, **54,** 840) of "cellulose" (such as filter paper and cotton) give considerable yields of the chloro- or bromo-derivatives of methylfurfural when they are heated with dry hydrogen chloride or bromide dissolved in an appropriate solvent. It was further shown that the formation of the bromo-derivative in any notable quantity is indicative of the presence of a *ketohexose* nucleus or grouping, and the existance of one or more such groupings in "cellulose" was consequently inferred. Recent experiments indicate that the same observations apply also to the *chloro*-derivative.

After treatment of cellulose in this manner with dry hydrogen chloride and complete removal of the methylfurfural derivative by washing repeatedly modification of Skraup's process, obtained two octacetyl derivatives, one melting at 228°–229° and the other melting at 196° and instantly converted into the first form by heating with acetic anhydride and sulfuric acid. Skraup[1] subsequently prepared the acetochloro derivative directly from cellulose, but was unable to obtain a biose from the acetyl modification with melting point of 200°. E. v. Hardt-Stremayr[2] found that the acetates of Maquenne and Goodwin and of Skraup are identical, the true melting point being 196°.

In the method of F. Klein,[3] for the preparation of cello-

with ether, a dark brown residue is left, which, in the case of filter paper, still shows a fibrous structure and amounts to about 90% of the material taken. If this residue is digested with warm water, a solution is obtained which gives all the reactions of *dextrose*. It is strongly dextro-rotatory, and with phenylhydrazine acetate, on heating, yields *glucosazone* (m. p. 204°–206°. N = 15.83, theory requiring 15.64 per cent.). On evaporating the solution to small bulk in a vacuum and adding alcohol, a syrup is at once precipitated, which solidifies on standing, and the solution continues to deposit crystalline crusts after a time. Mannose appears to be excluded from the fact that phenylhydrazine gives no precipitate in the cold even after standing for several hours.

Fifty grams of Swedish filter paper were treated in the manner above described, the solvent used being carbon tetrachloride, and the resulting chloromethylfurfural estimated by weighing the crystals. The residue was then extracted with water, and the dextrose estimated by means of Fehling's solution. The results gave chloromethylfurfural 3.1 gm., and dextrose 1.57 gm. At first sight, therefore, it would appear that the methylfurfural derivative is produced in excess. But it is found that when dextrose is treated in the same manner, a considerable portion is destroyed, leaving a black residue. A blank experiment was made with 5 gm. of dextrose under exactly similar conditions, with the result that the carbon tetrachloride extract weighed only 0.01 gm., and the residual sugar 2.2 gm. If it be assumed that the dextrose resulting from the action on cellulose is destroyed to a similar extent, the calculated amount of this sugar produced in the first experiment mentioned would be 3.54 gm. This, it will be seen, is approximately the quantity required (3.86 gm.) on the assumption that the chloromethylfurfural and dextrose are produced in *equal molecular proportions* (144.5:180).

These facts appear to be of special interest in relation to the work of *Skraup and König* (Ber. 1901, **34**, 1115), in which it is stated that the cellulose acetate obtained by the action of acetic anhydride and concentrated sulfuric acid on filter paper is an *octo-acetyl biose*, and that this on hydrolysis yields "cellose," $C_{12}H_{22}O_{11}$.

[1] Monatsh. 1905, **26**, 1415; abst. J. C. S. 1906, **90**, i, 67; Jahr. Chem. 1905–1908, II, 929.

[2] Wien. Akad. Ber. **116**, 2-b, 3; Monatsh. 1907, **28**, 63; abst. J. C. S. 1907, **92**, i, 389; Chem. Zentr. 1907, I, 1570; J. S. C. I. 1907, **26**, 482; Bull. Soc. Chim. 1908, (4), **4**, 4; Jahr. Chem. 1905–1908, II, 922; C. A. 1907, **1**, 2179. See also Hardt-Stremayr, Wien. Akad. Ber. **116**, II-b, 13; abst. Jahr. Chem. 1905–1908, II, 922.

[3] Zts. ang. Chem. 1912, **25**, 1409; abst. J. S. C. I. 1912, **31**, 713; Chem. Zentr. 1912, **83**, 1196; Chem. Tech. Rep. 1912, **36**, 532; Kunst. 1912, **2**, 311; C. A. 1913, **6**, 2303; J. C. S. 1912, **102**, i, 679. For pentaisovaleryl-, pentalauryl-,

biose octacetate, 10 gm. of cellulose are treated with 50 gm. of a mixture containing 80% of acetic anhydride and 20% of sulfuric acid, with special precautions to avoid local rise of temperature in the early stages. Subsequently the temperature may be raised to 35° or even 60° in order to accelerate the action. After 2–4 days the liquid sets to a mass of crystals; it is then diluted with glacial acetic acid and poured into a liter of water. The dried precipitate is recrystallized from three times its weight of 96% alcohol, the crystals forming long needles or leaflets. With proportions less than 3.5% of sulfuric acid or more than 30% no crystallization of the octacetate is obtained. Hydrocellulose gives the same results as cellulose and is more easily manipulated. The highest yield of cellobiose octacetate obtained is 60% of the weight of cellulose, or about 30% of the theoretical quantity. Although not more than about one-third of the monose groups of cellulose are obtained in the form of cellobiose octacetate, the evidence is quite in accordance with the view that all these groups are combined in the same manner. The by-products are of two kinds: acetylated cellulose dextrins and products soluble in water of the nature of mixed acetosulfuric esters. The acetates obtained from the alcoholic mother-liquors from the crystallization of the cellobiose octacetate, having specific rotations from +11° to +34,° are doubtless intermediate products of the breakdown of the cellulose molecule. The regular rise in the rotatory power and percentage of combined acetic acid, in these fractionated dextrin acetates, makes it almost certain that acetolysis proceeds in a regular series of steps. The products soluble in the aqueous liquors after precipitating the dextrin and cellobiose acetates have not been fully investigated; in certain circumstances, these water-soluble products amount to 40% of the weight of the cellulose, and their properties suggest that they are probably acetosulfates either of cellobiose or of dextrose. The experimental methods of investigating the various products of acetolysis include observation of melting point, hygroscopic moisture, specific

---

pentapalmityl-, pentastearyl-, pentacarbomethoxy-, tetracetylbenzoyl-, tetraacetysalicyl-, glucose, and heptaacetylbenzoylcellobiose, see G. Zemplen and E. Laszio, Ber. 1915, **48**, 915–26; abst. C. A. 1915, **9**, 2251. For data on Cellulase, see H. Euler, Zts. ang. Chem. 1912, **25**, 250; abst. C. A. 1912, **6**, 3516. de Bary, Bot. Zts. 1886, 377. M. Ward, Ann. Bot. 1888, **2**, 319. Schellenberg, Flora, 1908, **98**, 257. Brown and Morris, J. C. S. 1890, **57**, 453. Green, Phil. Trans. 1887, **39**, 179. C. Yllner, Zts. ang. Chem. 1912, **25**, 103.

rotatory power in chloroform solution, combined acetic acid, cupric reducing power and solubility of the free dextrins obtained on saponification. The combined acetic acid is best determined by hydrolysis with a mixture of equal volumes of sulfuric acid and water and titration of the volatile acid. Alkaline saponification with $N/2$ alcoholic sodium hydroxide for 12–18 hours must be resorted to when it is desired to investigate the free dextrins; the acetic acid thus found is 1%–3% higher than by acid hydrolysis. For the isolation of the free dextrins soluble in water, saponification with baryta water is more convenient. The melting points of the dextrin acetates are very doubtful and range about 100°; cellobiose octacetate alone melts sharply, at 222°; the combined acetic acid is 70.4%, and $[\alpha]_D = +41.7°$.

H. Ost and T. Katayama[1] acetylated cellulose, hydrocellulose, and alkali-cellulose both in presence of zinc chloride and of sulfuric acid, under similar conditions, the resulting acetates being examined as regards solubility in alcohol, acetone, and chloroform, and the dissolved fractions tested for rotatory power and acetic acid content. In the first series of experiments, 5 gm. of the cellulose were acetylated at 70° with 25 gm. of acetic acid, 25 gm. of acetic anhydride, and 2.5 gm. of zinc chloride; the acetates obtained from hydrocellulose and alkali-cellulose, after like periods, contained larger percentages soluble in acetone than the acetates of cellulose; in each case the percentage soluble in acetone increased with the period of acetylation, indicating hydrolysis. Both hydrocellulose and alkali-cellulose were completely esterified within two hours, while the cellulose required 20 hours. After 65 hours treatment, the acetates from cellulose contained 21.7 and 22.5% soluble in acetone, while after 2 hours the esters from hydrocellulose contained 18.9% and after 20 hours 32.8%, and those from alkali-cellulose after 2 hours' treatment 27.1% soluble in acetone. These acetone-soluble portions gave films which were either very brittle or non-elastic. In the second series of experiments the same quantities were used, but the zinc chloride was replaced by 0.5 gm. of sulfuric acid and acetylation was carried out at the ordinary temperature;

---

[1] Zts. ang. Chem. 1912, **25**, 1467; abst. J. S. C. I. 1912, **31**, 713; Jour. Ind. Eng. Chem. 1912, **4**, 701; Kunst. 1912, **2**, 311; Chem. Tech. Rep. 1912, **36**, 485; Wag. Jahr. 1912, II, 560; C. A. 1913, **6**, 2303; Chem. Zentr. 1912, II, 1199.

in these experiments only cellulose and hydrocellulose were used, and the ester mixtures from these appeared identical after 48 hours; the percentages soluble in acetone were 20.0 and 24.8, respectively. The specific rotatory power of the fractions soluble in chloroform from cellulose and hydrocellulose varied between —20.5° and —21.1°, and from alkali-cellulose from —21° to —22°; the figures for the corresponding portions soluble in acetone were —17.3 to —17.8°, and —21.8°. The acetic acid content of the chloroform- and acetone-soluble fractions agreed in all cases with that of cellulose triacetate, except that of cellulose acetylated in presence of zinc chloride for 65 hours, when it was slightly higher. In the third series of experiments, cellulose and hydrocellulose were acetylated in presence of sulfuric acid at 70°; in this case more than half the product was soluble in alcohol, and the remainder completely soluble in acetone; when 1 gm. of sulfuric acid was used instead of 0.5 gm., the products were almost completely soluble in alcohol, and consisted principally of cellobiose-octa-acetate; under suitable conditions this ester is converted into α-dextrose-penta-acetate, of m. p. 112.°

E. Knoevenagel[1] has shown that acetolysis occurs in the presence of many contact substances besides sulfuric acid, in the presence of acetic anhydride, and has intimately studied the effect of acetic anhydride upon benzolacetone in the presence of ferric chloride.

G. Zemplen[2] found that when cellulose and hydrocellulose

[1] Zts. ang. Chem. 1909, **22,** 281; abst. Chem. Ztg. 1909, **31,** 104; J. C. S. 1911, **100,** i, 179. See also "Dissertation on the Hydrolytic and Acetolytic Breaking up of Cellulose under the influence of Different Contact Substances," Heidelberg, 1911. W. Schleimann, "Cellobiose and the Acetolysis of Cellulose," Ztg. ang. Chem. 1912, **25,** 771; Ann. 1911, **378,** 366; abst. Bull. Soc. Chim. 1911, (4), **10,** 1346; C. A. 1911, **5,** 1276; Chem. Zentr. 1911, I, 807; J. S. C. I. 1911, **30,** 126.

[2] Zts. physiol. Chem. 1913, **85,** 180; abst. J. S. C. I. 1913, **32,** 651; J. C. S. 1913, **104,** i, 708; C. A. 1913, **7,** 3836; Chem. Zentr. 1913 II, 426. For bromacetocellobiose, iodoacetocellobiose and hepta-acetylcellobiose, see Fischer and G. Zemplen, Ber. 1910, **43,** 2536; abst. J. C. S. 1910, **98,** i, 718. According to G. Bertrand and M. Holderer (Compt. rend. 1909, **149,** 1385; abst. J. S. C. I. 1908, **27,** 102; cellose Z. Skraup and J. Koenig, Ber. 1901, **34,** 1115; Monatsh. Chem. 1901, **22,** 1011; J. S. C. I. 1901, **20,** 740) a biose produced by the partial hydrolysis of cellulose, is not hydrolyzed by maltase and sucrase. After contact, however, with an aqueous maceration of *Aspergillus niger* for about three days at 37° C., pure cellose is entirely transformed into dextrose. Emulsin and trehalase also hydrolyze it, but these diastases are not obtainable in sufficient purity to form definite conclusions from their action. The authors conclude in favor of the existence of a dias-

are subjected to acetolysis preferably under the conditions described by Klein, both yield practically the same amount (50–55%) of cellobiose octacetate. According to his results, amyloid is not identical with hydrocellulose, and hydrolysis by 70% sulfuric acid, even after prolonged action does not extend to the cellobiose groups, for the final product yielded no dextrose pentacetate as the result of the acetolysis.

H. Ost[1] found by the action of dilute sulfuric acid upon cellulose, that hydrocellulose is very readily formed, but not more than about one-half of the cellulose can be made to undergo total hydrolysis to dextrose by this means. Moreover, there appear to be no intermediate products (dextrins) between hydrocellulose and dextrose when cellulose is hydrolyzed by dilute acids. According to the author's experiments, neither cellulose nor hydrocellulose become perfectly anhydrous when dried at 100°–105°; the sample should be heated slowly up to that temperature and finally dehydrated at 120°–125°. Between that temperature and 130° or even 140°, purified cotton cellulose remains white and suffers no further loss of weight, but certain samples of hydrocellulose are slightly decomposed by heating at 125°–130°.

Hydrocellulose is less hygroscopic than cellulose. When both substances are corrected for the hygroscopic moisture expelled at 120,° elementary analysis fails to show any difference between cellulose and hydrocellulose. The quantity of water combining with the cellulose in this first stage of hydrolysis falls within the limits of analytical error. When cellulose is hydrolyzed by means of strong sulfuric acid, it forms the acid esters of a series of cellulose dextrins, which by heating at 120°, after dilution, may be almost quantitatively resolved into dextrose. Any "amyloid" precipitated by dilution must again be treated with strong sulfuric acid before it can be completely hydrolyzed. Sulfuric acid of 70% strength is a better reagent for the "sulfolysis" of cellulose than the more concentrated acid. When cellulose is acetylated by a mixture containing sulfuric acid as a

tase, cellase, distinct from maltase. For the partial hydrolysis of tunicate cellulose, see the topic "Animal Celluloses."

[1] Ann. 1913, **398**, 313; abst. J. S. C. I. 1913, **32**, 784; Kunst. 1913, **3**, 352; C. A. 1913, **6**, 3836; J. C. S. 1913, **104**, i, 446, 833, 1148; Chem. Zentr. 1913, II, 2035; Ber. 1913, **46**, 2995. See also Ost, Zts. ang. Chem. 1912, **25**, 1996; abst. Kunst. 1913, **3**, 330.

catalyst, the solution on further standing, loses its viscosity and a range of dextrin acetates is produced, terminating in cellobiose octacetate and dextrose pentacetate. These hydrolyzed products contain more combined acetic acid than cellulose triacetate.

The author has investigated the most favorable conditions for the total acetolysis of cellulose to dextrose acetates. The best results are obtained with a mixture of equal parts of acetic anhydride and glacial acetic acid containing 10 gm. of sulfuric acid per 100 cc. Cellulose is digested with about 11 times its weight of such a mixture at 18°–20° for 4–6 months. From the reaction-product a certain amount of cellobiose acetate crystallizes out; the liquid is poured into water and the dried precipitate is extracted with ether; the insoluble matter contains cellobiose acetate and the acetates of intermediate dextrins. The former separates on crystallization from 70% alcohol, while the dextrin acetates are precipitated from the mother liquors by water. The ethereal extract of the precipitate and the ethereal extract of the portion of the reaction product soluble in water contain the dextrose acetate; a portion of this crystallizes out as pentacetate and further quantities of pentacetate may be prepared by subsequent acetylation of the residual syrups with mixtures containing only traces of sulfuric acid. Of crystallized products, cellobiose and dextrose acetates, 60.6% of the theoretical quantity have been obtained from cellulose, but the residual syrups containing acetates soluble in ether but not crystallizable, bring the total yield of simple products to over 92% of the theoretical. These residual syrups are identical with those obtained in the acetylation of dextrose, and the author concludes that the cellulose molecule is entirely composed of dextrose residues.

He claims[1] the total hydrolysis of cellulose to dextrose has only been accomplished by way of its esters. After conversion into the sulfuric ester, cellulose may be completely resolved by "sulfolysis," by heating the solution with water at 120°, into its constituent hexose groups. In an analogous manner a similar resolution may be effected by "acetolysis" after conversion into the acetate. Hydrolysis of the cellulose complex must take place by the oxygen atoms, which unite the hexose residues by lactonic

---

[1] Chem. Ztg. 1912, **36**, 1099; abst. J. S. C. I. 1912, **31**, 980; Kunst. 1912, **2**, 412; Jour. Soc. Dyers, 1912, **28**, 369.

linkages, taking up each one molecule of water and forming two hydroxyl groups. Thus the 3 *mn* hydroxyls of a cellulose molecule made up of *mn* dextrose residues will become on hydrolysis *n* (3*m* + 2) hydroxyls, and a dextrin which may be produced, composed for instance, of 10 dextrose residues, will contain, not 30, but 32 hydroxyls, while the biose will contain 4 and the monose 5 hydroxyls per C_6 unit. This progressive hydrolysis can only be detected by elementary analysis in its later stages, but it is more sharply indicated by the increase in the combined acetic acid in the esters.

Thus cellulose triacetate contains 62.5% of acetic acid, the acetate of a dextrin, $C_{60}H_{102}O_{512}$ (with 32 hydroxyls) contains 64.4%, cellobioseoctacetate contains 70.8%, and dextrose pentacetate 76.9%. Cellulose may be converted into dextrose pentacetate in the following manner: 5 gm. of cellulose, 25 cc. of acetic anhydride, 25 cc. of acetic acid and 5.5 gm. of sulfuric acid are digested at 40°–45° for two days. The product is poured into water when it has reached a stage when a minimum precipitation (bioseacetate and humus matters) thereby results. The aqueous solution is exhausted with ether, which extracts a syrupy mixture of various acetates of dextrose. When this mixture is re-acetylated in the cold by acetic anhydride with only traces of sulfuric acid, a very large yield of pure dextrose-α-pentacetate, melting at 112°, is obtained.

According to J. Boeseken, J. van den Berg and A. Kerstjens[1] the acetylation of carbohydrates of high molecular weight requires a catalyst which forms an unstable compound with the hydroxyl group. Thus sulfuric, hydriodic, hydrobromic, and hydrochloric acids are active in the order named, corresponding with the order of stability of their compounds with the hydroxyl group. Of the catalysts examined, only hydrobromic acid, hydriodic acid, and acetyl iodide are comparable with sulfuric acid. The primary function of the catalyst is to act as a common solvent of the carbohydrates and the acetic anhydride, and the rate of acetylation is limited by the rate of diffusion of the acetylating mixture in the carbohydrate, which is much slower than the actual acetylation. The difference in the rates of acetylation of cellulose and starch

---

[1] Rec. Trav. Chim. Pays-Bas, 1916, **35**, 320; abst. J. S. C. I. 1916, **35**, 464; Zts. Chem. Ind. Koll. 1917, **21**, 160; J. C. S. 1916, **110**, ii, 466.

is probably due to the difference in the surface exposed, and the influence of catalysts on both reactions is approximately of the same order. The relative surface of colloidal carbohydrates is probably approximately measured by the velocity of acetylation, because this depends on the diffusion of the acetylating mixture in the carbohydrates. The chemical reaction consists of a succession of processes of acetylation and hydrolysis (or acetolysis). It is doubtful whether mono- and di-acetates of cellulose have ever been obtained directly since if the reaction is stopped before the cellulose has all dissolved, the acetate in solution is the triacetate, and the undissolved cellulose contains practically no combined acetic acid. If the general formula of the polyglucoses is written $(C_6H_{12}O_6)_n$—$(n-1)H_2O$, *n* becomes lower as the molecule is hydrolyzed, and the acetyl number increases gradually from 62.5 (for cellulose triacetate) to 77 (for dextrose pentacetate). A proportional figure for the degree of acetolysis is obtained by assuming that the carbohydrate molecule $(C_6H_{12}O_6)_n$—$(n-1)H_2O$ combines with $(3n + 2)$ molecules of acetic acid, forming the triacetate of molecular weight $(162n + 18) + (3n + 2)42$. The acetyl number is then $\frac{1000\,(3n + 2)}{48n + 17}$ from which *n* can be calculated. It gives the average number of dextrose groups in the products of hydrolysis. It is probable that as long as the acetyl number is about 62.5, the cellulose has only split into groups of approximately equal size, without forming simple molecules such as cellobiose acetate or dextrose pentacetate; otherwise there would be a large proportion of the product soluble in alcohol and ether. When the acetyl number begins to exceed 62.5, *n* increases very rapidly with time, indicating profound acetolysis of the molecule.

E. Bourquelot and M. Bridel[1] find cellobiose or cellose to be isomeric with gentiobiose and maltose. It is dextrogyrous with multiple rotation reaching 34° at stability. One mgm. cellobiose precipitates 1.38 mgm. Cu. It is hydrolyzed by emulsin or better by an enzyme, cellobiase, whose specificity has been de-

---

[1] Compt. rend. 1919, **168**, 253, 701, 1016; abst. C. A. 1919, **13**, 1209, 1486, 2010. G. Bertrand and M. Holderer, Ann. inst. Pasteur, 1910, **24**, 180; Bull. Soc. Chim. 1910, **7**, 177; abst. C. A. 1910, **4**, 1870, 1994, 3240. Compt. rend. 1910, **150**, 285; abst. C. A. 1910, **4**, 1994.

termined by Bertrand and Holderer. To each of two solutions of glucose containing 30 to 50 gm. respectively, in 100 cc. H_2O, one gm. of emulsin was added and the synthesizing reaction allowed to proceed at ordinary temperature to equilibrium, when, after convenient dilution, top yeast was added to destroy the remaining glucose. This being done, the solutions were filtered, evaporated, to dryness under reduced pressure, and found to be 15.7° and 15.9° respectively, showing the reactions to have been the same. From these residues some gentiobiose with a rotation of 10.2° was removed, showing that other sugars with a higher rotation than 15° were mixed with the gentiobiose. If the residue, 42 gm.[1] is dissolved in 60 cc. H_2O and 40 cc. absolute alcohol added a voluminous precipitate is formed. The liquid is decanted and the residue taken up at boiling, first with 100 cc. 95% alcohol, then with 200 cc. 90% alcohol. This last solution was decanted and after 15 days primed by rubbing the walls of the beaker with a rod to which adhered traces of cellobiose chemically prepared. The crystals produced showed the exact microscopic appearance of chemically prepared cellobiose and a multirotation of 12.06°, 25.74°, and 30.50° after 4 minutes, and stabilization, respectively, one mgm. precipitated 1.389 mgm. Cu, and 1. gm. treated with 3% sulfuric acid gave 1.07 gm. reduced sugar. It, therefore, appears established that gentiobiase, cellobiase and glucosidase exercise simultaneously their synthesizing action in a solution of glucose.

Hydrolysis and Saccharification. The study of the hydrolysis of cellulose has engaged the attention of chemists for over a century, as far back as 1797. A. Fourcroy and Vauquelin[2] having published a memoir upon this subject, which twenty-two years later was made the basis of an investigation by H. Braconnot.[3] The interest in the problem is due not only to the possible economic utilization of the resulting products, but also to the theoretical

[1] Cf. C. A. 1919, **13**, 1209, line 20.

[2] Ann. Chim. Phys. 1797, (1), **23**, 186, 203; Nicholson J. 1797, I, 385; Trommsdorff, J. Pharm. 1797, **6**, 172, 189.

[3] Ann. Chim. Phys. 1819, (2), **12**, 172; abst. Dingl. Poly. 1820, **1**, 312; 1827, **25**, 81; Gilb. Ann. 1819, **63**, 348; Edin. Phil. J. 1820, **2**, 363; J. de Pharm. 1820, **6**, 416; Quart. J. Sci. 1820, **8**, 386; Schw. J. 1819, **27**, 328. Tilloch, Phil. Mag. 1820, **55**, 53, 118. See also Nancy, Trav. Soc. Sci. 1819–1823, 66; Gilb. Ann. 1822, **70**, 389; Giorn. Arcad. 1820, **6**, 277; Quart. J. Sci. 1820, **9**, 392.

importance of the reactions as possibly furnishing a satisfactory solution of the structure of the cellulose complex, for the products obtained were crystalline and hence readily purified in contradistinction to cellulose, which in all forms is amorphous.

The work of Braconnot was followed by that of J. Arnould,[1] M. Pettenkofer,[2] Tribouillet,[3] Pelouze,[4] G. Melsens,[5] F. Varrentrapp,[6] A. Payen,[7] H. Ludwig,[8] H. Tauss,[9] J. Matheus,[10] C. Amos and W. Anderson,[11] J. Poumarede and L. Figuer,[12] as well as,

[1] Compt. rend. 1854, **39**, 807; Dingl. Poly. 1854, **134**, 219; Poly. Notiz. 1855, 31; Wag. Jahr. 1855, **1**, 221; Instit. 1854, 366; Arch. ph. Nat. **27**, 331. See also Tribouillet, Mon. Ind. 1854, 908; Dingl. Poly. 1854, **134**, 316; Poly. Centr. 1855, **21**, 128; Wag. Jahr. 1855, **1**, 221. Melsens, Genie. Ind. 1855, 106; abst. Dingl. Poly. 1855, **138**, 426.

[2] Bayer Kunst. u. Gewerbebl. 1855, 136; Dingl. Poly. 1855, **136**, 387; Poly. Centr. 1855, **21**, 955; Poly. Notiz. 1855, **10**, 161; Wag. Jahr. 1855, **1**, 222; Poly. Centr. 1855, **21**, 955; Pharm. Centr. 1855, **26**, 557.

[3] Mon. Ind. 1854, 1908; Dingl. Poly. 1854, **134**, 316; Poly. Centr. 1855, **21**, 128; Wag. Jahr. 1855, **1**, 221; Compt. rend. 1854, **39**, 980.

[4] Compt. rend. 1859, **48**, 327, 1027; abst. Mon. Sci. 1859–1860, **2**, 86, 131; Poly. Centr. 1859, **25**, 976; Dingl. Poly. 1859, **151**, 394; Jahr. Chem. 1859, **12**, 533; J. pharm. 1859, **35**, 209; Instit. 1859, 49; Rep. Chim. Pure, **1**, 272. See also Weil, Compt. rend. 1859, **48**, 1027. Payen, Dingl. Poly. 1855, **138**, 58. W. Stein, Poly. Centr. 1855, **21**, 429. A. Hofmann and Redwood, Pharm. J. Trans. **14**, 556; **15**, 28; Chem. Soc. Quart. J. 1855, **8**, 120. Robinet, J. Pharm. (3), **27**, 191. Campani, Cimento, **2**, 210. Rabourdin, J. Pharm. (3), **28**, 68; Vierteljahrschr pr. Pharm. **5**, 406; Jahr. Chem. 1854, **7**, 797. Walz, N. Jahr. Pharm. **3**, 217. H. Ludwig, Arch. Pharm. (2), **82**, 22; Pharm. Centr. 1855, **26**, 512. Bordier, Dingl. Poly. 1855, **136**, 387.

[5] Genie industr. 1855, 106; Dingl. Poly. 1855, **138**, 426; Wag. Jahr. 1855, I, 221; Poly. Centr. 1856, **22**, 873.

[6] Mitth. f. Gewerbever. des Herzogthums, 1865, 70; Dingl. Poly. 1866, **181**, 233; Wag. Jahr. 1866, **12**, 466; Braunschweig. 1866, 73; Deut. Ind. 1866, 366; Poly. Centr. 1866, **32**, 1150.

[7] Compt. rend. 1867, **64**, 1167; Dingl. Poly. 1867, **185**, 308; Chem. Centr. 1868, **13**, 20; Jahr. Chem. 1867, 952, 953; Mon. Sci. 1868, **10**, 322; Poly. Centr. 1867, **33**, 1351. See also Payen, Ann. Chim. Phys. 1866, (4), **7**, 382; Zts. Chem. 1866, 334. Bachet and Marchard, Jahr. Chem. 1866, **19**, 663; Van Tieghem, Compt. rend. 1863, **56**, 963; abst. Jahr. Chem. 1863, **16**, 565; Chem. Centr. 1863, **34**, 950.

[8] Zts. f. deutsche Landwirthe, 1855, 192; Dingl. Poly. 1855, **138**, 80; Poly. Centr. 1855, **21**, 1085; Poly. Notiz. 1855, **10**, 286; Wag. Jahr. 1855, **1**, 223.

[9] Dingl. Poly. 1889, **273**, 276; 1890, **276**, 411; abst. Chem. News, 1890, **61**, 169; J. S. C. I. 1889, **8**, 913; Mon. Sci. 1890, **55**, 164; Ber. 1889, **22**, R, 769; Chem. Centr. 1889, **60**, II, 444; Chem. Ind. 1889, **12**, 514; Chem. Tech. Rep. 1890, II, 105; Jahr. Chem. 1889, **42**, 2838; Wag. Jahr. 1889, **35**, 1; Apothker Ztg. 1890, 232; J. S. C. I. 1890, **9**, 883; Mon. Sci. 1891, **38**, 1264; Ber. 1891, **24**, R, 277; Chem. Centr. 1890, **61**, II, 187; Jahr. Chem. 1890, **43**, 2189, 2873; 1891, **44**, 2811; Wag. Jahr. 1890, **36**, 1148.

[10] Dingl. Poly. 1893, **287**, 91; abst. Jahr. Chem. 1893, **46**, 647.

[11] Mechanics Mag. 1866, 341; abst. Dingl. Poly. 1867, **184**, 308; Jahr. Chem. 1867, **20**, 953. Chaudet and Delamure-Debouteville, F. P. 123556, 1878; abst. Chem. Ind. 1878, **1**, 421; Mon. Sci. 1879, **21**, 1042.

[12] Compt. rend. 1846, **23**, 918; 1847, **25**, 17; abst. J. prakt. Chem.

J. Sacc,[1] F. Schulze,[2] H. Mohl,[3] E. Fremy[4] with Terreil[5] and Urbain,[6] F. Bente,[7] J. Erdmann,[8] A. Stutzer,[9] H. Kolbe,[10] Flechsig,[11] G.

1847, **42,** 25; Berz. Jahr. 1849; **28,** 340; Jahr. Chem. 1847–1848, **1,** 797; Rev. Sci. 1847, **14,** 68; Ann. 1847, **64,** 387; Annuaire de Chim. 1847, 453; J. Pharm. 1847, (3), **11,** 81; Rep. Pharm. (2), 47, 344; Soc. Philom. Proc. Verb. 1846, 130.

[1] Ann. Chim. Phys. 1849, (3), **25,** 218; abst. Jahr. Chem. 1849, **2,** 473, 688, 704; J. prakt. Chem. 1849, **46,** 430; Pharm. Centr. 1849, **20,** 235; Chem. Gaz. 1849, 274. See also J. Sacc, Ann. Chim. Phys. 1849, (3), **27,** 473; J. prakt. Chem. 1850, **49,** 296; Pharm. Centr. 1850, **21,** 91; Jahr. Chem. 1849, **2,** 704; J. Pharm. 1849, **16,** 293.

[2] Chem. Centr. 1857, **28,** 321; Jahr. Chem. 1857, **10,** 491. See also Mitscherlich, Berl. Acad. Ber. 1850, 102; Ann. 1850, **75,** 305; J. prakt. Chem. 1850, **50,** 144; Pharm. Centr. 1850, **21,** 385; Chem. Gaz. 1851, 61; Instit. 1850, 228; Jahr. Chem. 1850, **3,** 541. E. Schulze, Ber. 1890, **23,** 2579; abst. J. C. S. 1890, **58,** 1456; Chem. Centr. 1890, **61,** I, 650; J. S. C. I. 1890, **19,** 1051.

[3] Flora, 1840, **23,** 609, 625; Ann. Sci. Nat. 1841, **15,** 38.

[4] Compt. rend. 1859, **48,** 202, 862; 1876, **83,** 1136. N. J. Pharm. **35,** 81; abst. Rep. Chim. Pure, 1859, **1,** 269; Compt. rend. 1859, **48,** 325, 360, 667, 862; J. Pharm. **35,** 321, 401; abst. Inst. 1859, 121, 151; Rep. Chim. Pure, 1859, **1,** 357, 433; Pharm. Vierteljahr. **9,** 221; N. J. Pharm. Inst. 1859, 357; Rep. Chim. Pure, 1859, **1,** 602; Chem. Centr. 1860, 4; Compt. rend. 1859, **49,** 561; Jahr. Chem. 1859, **12,** 529, 530, 532, 533, 534, 537, 540; Bull. Soc. Chim. 1877, **28,** 174; Ber. 1877, **10,** 90.

[5] Compt. rend. 1868, **66,** 456; Bull. Soc. Chim. 1868, **9,** 436; Ber. 1877, **10,** 90; J. pharm. Chim. 1868, **7,** 241; abst. Chem. Centr. 1868, **39,** 616; Jahr. Chem. 1868, **21,** 762.

[6] Compt. rend. 1882, **94,** 108; Ann. sci. nat. 1882, (6), **13,** 353; abst. J. C. S. 1882, **42,** 708; J. S. C. I. 1882, **1,** 113; Bull. Soc. Chim. 1882, **37,** 409; Jahr. Chem. 1882, **35,** 1150.

[7] Ber. 1875, **8,** 476; Landw. Versuchstat. 1876, **19,** 164; abst. Bull. Soc. Chim. 1876, **25,** 278; Chem. Centr. 1875, **46,** 392; Chem. Tech. Rep. 1875, **14,** I, 16; Dingl. Poly. 1875, **217,** 235; Jahr. Chem. 1875, **28,** 785; Wag. Jahr. 1875, **21,** 1045; Jahr. rein Chem. 1875, **3,** 382.

[8] Ann. 1866, **138,** 1; Ann. Suppl. 1867, **5,** 223; abst. Bull. Soc. Chim. 1866, (2), **6,** 340; 1868, (2), **10,** 295; Chem. Centr. 1866, **37,** 401; 1868, **39,** 395; Jahr. Chem. 1867, **20,** 672, 738; Zts. Chem. 1868, 155, 245; J. Pharm. (4), **3,** 478. Jahr. rein Chem. 1875, **3,** 382.

[9] Ber. 1875, **8,** 575; abst. Bull. Soc. Chim. 1876, **25,** 471; Jahr. Chem. 1875, **28,** 822. A. Stutzer, D. R. P. 215273, 1908; Pap. Ztg. 1909, **34,** 3758; abst. C. A. 1910, **4,** 628; Chem. Zentr. 1909, **80,** II, 1783; Chem. Ztg. Rep. 1909, **33,** 606; Wag. Jahr. 1909, **55,** I, 291. F. P. 402871, 1909; abst. J. S. C. I. 1909, **28,** 1323. Des. Deut. Naturforscher und Aerzte Sept. 1909; abst. Zts. ang. Chem. 1909, **22,** 1999; J. S. C. I. 1909, **28,** 1162; Bull. Soc. Chem. 1910, (4), **6,** 222; Jahr. Chem. 1909, **62,** II, 387; Meyer Jahr. Chem. 1909, **19,** 323.

[10] J. prakt. Chem. 1880, (2), **21,** 443; **22,** 112; abst. Oest. Ung. W. u. Agr. Ztg. **11,** 241; J. C. S. 1880, **38,** 520; 1881, **40,** 212; Bull. Soc. Chim. 1880, **34,** 96; Ber. 1880, **13,** 1142, 1759; Chem. Centr. 1880, **51,** 358, 501; Chem. Tech. Rep. 1880, I, **19,** 444; Chem. Ztg. 1880, **4,** 488; Jahr. Chem. 1880, **33,** 1063; Jahr. rein Chem. 1880, **8,** 369; Wag. Jahr. 1880, **26,** 454; Zts. Chem. Grossgewerbe, 1860, **5,** 119, 135, 151, 308.

[11] Zts. physiol. Chem. 1883, **7,** 523; abst. Ber. 1883, **16,** 2508; Chem. Tech. Rep. 1883, **22,** II, 144; Jahr. Chem. 1883, **36,** 1363; Wag. Jahr. 1883, **29,** 681; Tech. Chem. Jahr. 1883–1884, **6,** 275; Zts. Deut. Spiritusfabr. 1883, 805.

Mulder,[1] F. Hoppe-Seyler,[2] T. Thomsen,[3] F. Koch,[4] A. Ihl,[5] M. Singer,[6] and others[7] previous to 1895. Notwithstanding the

---

1. Scheik. Onderzoek, **2,** 76; abst. J. prakt. Chem. 1844, **32,** 336; Ann. 1841, **39,** 150.

2. Ber. 1871, **4,** 15; abst. J. C. S. 1871, **24,** 226; Chem. Centr. 1871, **42,** 84; Jahr. Chem. 1871, **24,** 476; Bull. Soc. Chim. 1871, **15,** 98; Chem. News, 1871, **23,** 131. See G. Foch, Chem. Ztg. 1913, **37,** 1221. R. McKee, Paper, 1919, **25,** 25, 34.

3. J. prakt. Chem. 1879, **127,** 146; abst. Ind. Blätter 1879, 402; Archiv. Pharm. **9,** 557; J. C. S. 1879, **36,** 613; J. S. C. I. 1883, **2,** 89; Bull. Soc. Chim. 1880, (2), **33,** 494; Ber. 1879, **12,** 1012; Chem. Centr. 1879, **50;** Dingl. Poly. 1879, **233,** 413; Jahr. Chem. 1879, **32,** 896; Jahr. rein Chem. 1879, **7,** 503; Wag. Jahr. 1879, **25,** 1155. See also Scheibler, Ber. 1873, **6,** 612; abst. Jahr. Chem. 1873, **26,** 829.

4. Pharm. Zts. Russ. **25,** 619, 635, 651, 667, 683, 699, 730, 747, 763; abst. Ber. 1887, **20,** 145; Wag. Jahr. 1887, **33,** 1.

5. Chem. Ztg. 1885, **9,** 231, 451, 485; 1887, **11,** 19; abst. Chem. News, 1885, **51,** 114; J. C. S. 1885, **48,** 694; 1887, **52,** 534; J. S. C. I. 1887, **6,** 306; Ber. 1885, **18,** 128; 1887, **20,** 77 R; Chem. Centr. 1885, **56,** 761; Chem. Ind. 1888, **11,** 188; Chem. Tech. Rep. 1885, **24,** I, 258; II, 17; 1887, **26,** II, 329; Dingl. Poly. 1887, **266,** 597; Jahr. Chem. 1887, **40,** 2642; 1885, **38,** 1977; 1886, **39,** 1971. See also H. Molisch, Monatsh. Chem. 1886, **7,** 198; abst. Jahr. Chem. 1886, **39,** 1971, 2172; Dingl. Poly. 1886, **261,** 135.

6. Monatsh. 1882, **3,** 396; abst. J. C. S. 1882, **42,** 1122; J. S. C. I. 1882, **1,** 404; 1883, **2,** 89; Ber. 1882, **15,** 2272; Chem. Tech. Jahr. 1883, **22,** I, 243; Chem. Ztg. 1882, **6,** 603, 813; Wag. Jahr. 1882, **28,** 1060; Akad. Wissensch. Wein, 1882, 100; Tech. Chem. Jahr. 1892–1893, **5,** 212.

7. T. Seliwanoff, Ber. 1887, **20,** 181; abst. J. C. S. 1887, **52,** 459; Bull. Soc. Chim. 1887, (2), **48,** 135; Ber. 1887, **20,** 181; Chem. Ztg. 1887, **11,** 1486; Jahr. Chem. 1887, **40,** 2301; Landw. Ver.-Stat. **34,** 414. See also Chem. Ztg. 1885, **9,** 231. C. Wurster, Ber. 1887, **20,** 808, 3195; abst. J. C. S. 1887, **52,** 620; J. S. C. I. 1887, **6,** 565; Chem. Ind. 1888, **11,** 90; Chem. Tech. Rep. 1887, **26,** I, 188; II, 350; Jahr. Chem. 1887, **40,** 2467; Industriblatter, 1887, 119. E. Siegle, J. prakt. Chem. 1856, **69,** 148; Poly. Centr. 1856, **22,** 206; Wag. Jahr. 1856, **2,** 225. Roy, Ann. Soc. Linn. Paris, 1826, 219; Jour. f. oeken Chem. **1,** 215. Baer, Physikal. Lexicon, 1859, **6,** 849; Wag. Jahr. 1859, **5,** 401. Koerner, Diss. Dresden, 1907; Zts. ang. Chem. 1908, **21,** 2353. Gottlieb, J. prakt. Chem. 1883, (2), **28,** 385. Harpf, Pap. Ztg. 1891, 1845. Chudiakow, Landw. Jahr. 1894, **23,** 391. Giltay and Anderson, Jahr. Wiss. Bot. 1894, **26,** 543. Hansen, Medd. Carlsberg Labor. 1881, **2.** Iwanowsky, Bot. Centr. 1894, **58,** 344. Pederson, Pap. Ztg. 1890, 422.

For data on obtaining ethyl alcohol from sulfite solution as in wood pulp manufacture, consult, E. Haegglund, Pulp Paper Mag. **15,** 1125, 1157; E. Hendrick, Met. Chem. Eng. 1918; Papers Makers Monthly, 1918, **56,** 136; Paper, **22,** No. 4, p. 13. A. White and J. Rue, Paper Makers Monthly, 1917, **55,** 109, 146; Met. Chem. Eng. 1917, **9,** 182. G. Stlele, Worlds Paper Trade Rev. **66,** No. 25, p. 12. E. Oman, Pap. Fab. **13,** 534. V. Krieble, Paper, **23,** No. 23, p. 153; Pulp Paper Mag. **17,** 116.

Paper Makers Monthly, 1918, **56,** 136, 230, 235, 238, 359. Can. Chem. J. **2,** 211. Paper, **21,** No. 17, p. 16, 30; No. 18, p. 13; No. 19, p. 11; No. 20, p. 15. V. Krieble, Paper, Ann. Conv. No. 1919, **23,** 153; abst. J. S. C. I. 1919, **38,** 571-A F. Storer, Bull. Bussey Institution, 1900, **2,** (9); abst. J. S. C. I. 1901, **20,** 822. G. Pradel, F. P. 385015, 1907; abst. J. S. C. I. 1908, **27,** 516. G. Mezzadroli, Boll. Chim. Farm. 1918, **57,** 360–62; abst. J. S. C. I. 1919, **38,** 50-A. F. La Forge, U. S. P. 1288429, 1918; abst. J. S. C. I. 1919, **38,** 154-A. R. Kocher, E. P. 107219, 1916 (appl. No. 7339 of 1916); abst. J. S. C. I. 1917, **36,** 973. H. Landmark, First Addn. dated May 20, 1914 to F. P.

extensive nature of this pioneer work, but little real progress had been made toward establishment of the data accumulated upon a firm commercial manufacturing basis.

The most complete study of the saccharification of cellulose published up to that time is contained in a series of papers by E. Simonson in 1898,[1] who embodied his results in a patent.[2] He worked only on wood cellulose with the objective of the manufacture of industrial ethyl alcohol,[3] and found the most favorable conditions for the saccharification of 40 gm. of celluose to be a 2 hours digestion at 6–8 atmospheres pressure with 1080 cc. of 0.5% sulfuric acid, longer digestion causing a serious destruction of sugar. His results are epitomized in the following two tables, in which table 10 shows the amounts of *d*-glucose formed with sulfuric acid of varying concentrations after four hours treatment under the pressures stated:

456871, 1913. (J. S. C. I. 1913, **32**, 1063); abst. J. S. C. I. 1915, **34**, 488. Chem.-Ztg. 1915, **39**, 98–99; abst. J. S. C. I. 1915, **34**, 275. F. P. 456871, 1913; abst. J. S. C. I. 1913, **32**, 1063. T. Norton, U. S. Cons. Reps. Nov. 1911; abst. J. S. C. I. 1911, **30**, 1466. F. Kressmann, J. I. E. C. 1915, **7**, 920–923; abst. J. S. C. I. 1915, **34**, 1221. J. I. E. C. 1914, **6**, 625–630; abst. J. S. C. I. 1914, **33**, 1914. Junien, Bull. Assoc. Chim. Sucr. 1914, **31**, 500–501; abst. J. S. C. I. 1914, **33**, 213. E. Hägglund, J. prakt. Chem. 1915, **91**, 358–364; abst. J. S. C. I. 1915, **34**, 975.

[1] Zts. ang. Chem. 1898, **12**, 195, 219, 962, 1007; 1903, **16**, 572; Pap. Ztg. 1903, **28**, 572, 1787; J. C. S. 1896, **70**, i, 331; 1899, **76**, i, 471; J. S. C. I. 1898, **17**, 365, 481; 1898, **17**, 1164; Chem. Centr. 1898, **69**, I, 808; II, 144, 1140; Zts. ang. Chem. 1903, **16**, 572.

[2] D. R. P. 92079, 1894; abst. Chem. Centr. 1897, **68**, II, 559; Wag. Jahr. 1897, **43**, 978. E. P. 10762, 1895; Ber. 1897, **29**, 1035; Chem. Centr. 1896, 670; Chem. Ztg. 1896, **20**, 887; Pap. Ztg. 1896, **21**, 460. Norsk teknisk Tidskrift, 1895, 65. See Swed. P. 28551, 1907. Zts. ang. Chem. 1898, **11**, 219; abst. J. S. C. I. 1898, **17**, 365, 481. See also Ann. 1819, **12**, 172; Dingl. Poly. 1820, **1**, 312; 1827, **25**, 81; 1854, **134**, 219, 316; 1856, **136**, 187; 1855, **138**, 79, 80, 426; 1859, **151**, 394; 1866, **181**, 233; 1867, **185**, 308; 1889, **273**, 276; 1893, **287**, 91. Wag. Jahr. 1855, **1**, 200, 220; 1856, **2**, 225, 242; 1859, **5**, 40, 401. Zts. f. Spirit. Ind. 1883, (7). Lindsay, Inaug. Dissertation, 1891.

[3] See "Cellulose as a Polysaccharide," J. Briggs, J. S. C. I. 1909, **28**, 340; abst. C. A. 1909, **3**, 1589; Bull. Soc. Chim. 1909, (4), **6**, 1028; Rep. Chim. 1909, **9**, 370; Chem. Zentr. 1909, **80**, II, 270; Chem. Ztg. Rep. 1909, **33**, 257, 313; Jahr. Chem. 1909, **62**, II, 382; Meyer Jahr. Chem. 1909, **19**, 217; Zts. ang. Chem. 1909, **22**, 2300. Lassar-Cohn, Allg. Produktenzeit. **8**, 1; Chem. Zentr. 1918, **89**, II, 778; C. A. 1919, **13**, 3034.

TABLE XVI.—CELLULOSE TO GLUCOSE.

Pressure in Atmospheres	Sulfuric Acid			
	0.15%	0.3%	0.45%	0.6%
1.3	....	2.5	2.7	3.1
2.1	....	6.6	8.6	10.6
2.7	....	9.3	11.3	12.6
4.0	....	16.4	....	20.3
6.0	21.5	28.0	30.7	43.9
8.0	30.5	38.4	45.0	33.3
9.0	....	43.1	....	....
10.0	35.0	36.6	30.0	18.0
12.0	38.4	....	....	....
14.0	20.0	....	....	....

TABLE XVII.—CELLULOSE TO GLUCOSE (2.7 ATMS. PRESSURE)

Hours	Percentage of Sugar, with Sulfuric Acid of		
	0.3%	0.45%	0.6%
4	9.3	11.3	12.6
6	11.3	13.6	15.0
8	12.6	15.3	17.4

From the best of his experiments (an exceptional case), he claims to have obtained 45% of sugar and 44% of residue, which residue upon further treatment yielded 27% of sugar, but he does not appear to have corroborated this experiment by duplicating the work. He was the first to determine the factors which influence the hydrolysis of cellulose, and these are (a) pressure, (b) amount of water present, (c) length of time for maximum sugar formation, and (d) correct acidity. On a semi-manufacturing scale he determined the most favorable conditions to be as follows: The cellulose in the form of fine sawdust is mixed with 0.5% sulfuric acid in the ratio of wood to liquid 1 to 4, and is heated in an autoclave for 15 minutes at a pressure of 9 atmospheres, the sugar being then extracted from the residue. The sugar was not separated as such, but used directly after neutralization for the production of alcohol by fermentation. Yields of alcohol equivalent to 25 gallons of absolute alcohol per ton of dry sawdust are stated to have been obtained. It is usual in the hydrolysis of cellulose with sulfuric acid on the industrial scale, not to recover as such the sugar formed, but to ferment it directly into ethyl alcohol, the conditions under which the hydrolysis is carried out, influencing of course, the nature of the sugar formed and the ultimate yield of alcohol obtained.

The results of Simonsen—admittedly the most reliable—have been called in question by Koerner,[1] who has pointed out that Simonsen's yields of sugar were determined only by the cupric reducing power of the extracts, which is open to criticism. Furthermore Simonsen's extracts were not completely fermentable. Koerner, working along similar lines, obtained a yield of 12–18% of alcohol from wood cellulose corresponding to (say) 26% of dextrose. From "hydrocellulose" was obtained 18% alcohol, but the source of the hydrocellulose is not stated. Simonsen and Koerner conducted their researches, bearing in mind the utilitarian side of the question, and their work therefore, as has been pointed out by J. Briggs, lacks "the scientific value of a contribution to the theory of the constitution of the cellulose aggregate." The yield of alcohol theoretically possible from 100 gm. dry cellulose is 56.9 gm. and as under the most favorable conditions not over 25% of the theoretical quantity has been obtained by the simple hydrolysis of cellulose, it appears probable that of the entire cellulose complex, only a portion is capable of hydrolysis and conversion into fermentable sugar.

Braconnot and many of his successors proceeded by employing sulfuric acid of such a concentration that its first action in the cold is one of solution due to esterification. A. Stern[2] has

[1] Ztg. ang. Chem. 1908, **21**, 2353; Pap. Ztg. 1908, **33**, 3702; C. A. 1909, **3**, 484; J. S. C. I. 1908, **27**, 1216; Bull. Soc. Chim. 1908, (4), **6**, 230; Mon. Sci. 1909, **70**, 326; Chem. Zentr. 1908, **79**, II, 2049; Chem. Ztg. Rep. 1909, **32**, 692; Jahr. Chem. 1905–1908, II, 179; Meyer Jahr. Chem. 1909, **18**, 392; Wag. Jahr. 1909, **54**, II, 339. See also L. Roth and W. Gentzen, D. R. P. 147844; abst. Zts. ang. Chem. 1903, **16**, 244; Chem. Centr. 1904, **75**, I, 410; Jahr. Chem. 1904, **57**, 878; Chem. Ztg. 1904, **28**, 66; Wag. Jahr. 1904, **50**, II, 370; Mon. Sci. 1909, **70**, 327. See Aktiebolaget Ethyl, U. S. P. 1042332, 1050723, 1912. F. P. 446717, 446718, 1912; abst. J. S. C. I. 1912, **31**, 1075; 1913, **32**, 133, 192, 377.

[2] Proc. Chem. Soc. 1894, 186; J. C. S. 1895, **67**, 74; abst. J. S. C. I. 1894, **13**, 1230; Bull. Soc. Chim. 1896, (3), **16**, 1081; Ber. 1895, **28**, R, 462; Jahr. Chem. 1895, **48**, 1358; Meyer Jahr. Chem. 1895, **5**, 145, 524; Chem. News, 1894, **70**, 267; Chem. Centr. 1895, **66**, I, 29; Jahr. Chem. 1894, **47**, 1132. Proc. Chem. Soc. 1904, **20**, 43; J. C. S. 1904, **85**, 336; abst. Chem. News, 1904, **89**, 117; J. S. C. I. 1904, **23**, 265; Bull. Soc. Chim. 1904, **32**, 1175; Chem. Centr. 1904, **75**, I, 934, 1405; Chem. Ztg. 1904, **28**, 246; Jahr. Chem. 1904, **57**, 1161. In this connection see Proc. Chem. Soc. 1904, **20**, 90; J. C. S.

pointed out that in this manner the acid-sulfuric esters of a series of dextrin-like bodies are formed which on prolonged boiling in presence of dilute sulfuric acid are gradually hydrolyzed to dextrose. Stern has fractionated these esters and determined the cupric reducing and specific rotatory power of each fraction, the series chemically being analogous to the maltodextrin series of starch products. The "cellulose sulfuric acids" of Stern are non-reducing bodies, and the yields of barium cellulose sulfates from which all his deductions were made, never accounted for as much as half of the original cotton cellulose operated upon. J. Lindsey and B. Tollens[1] isolated 3.5% of crystalline dextrose from wood cellulose by this method, and Ernest[2] obtained about 4% of a dextrose syrup from ramie cellulose in the same manner.

G. Eckstrom[3] records a conversion of 55%–75% of dextrose by heating the cellulose in an autoclave for 0.5–5 hours at a pressure of from 3 to 8 atmospheres. In obtaining alcohol from waste sulfite

---

1904, **85**, 691; abst. Chem. News, 1904, **89**, 235; J. S. C. I. 1904, **23**, 557; Bull. Soc. Chim. 1904, **32**, 1301; Rep. Chim. 1904, **4**, 293; Chem. Centr. 1904, **75**, I, 1557; Jahr. Chem. 1904, **57**, 1161. See also M. Hoenig and S. Schubert, Monatsh. 1885, **6**, 708; 1886, **7**, 455; abst. Wein. Akad. Ber. **92**, (2 Abth.) 737; Bull. Soc. Chim. 1886, (2), **46**, 517; Ber. 1885, **18**, 614; Jahr. Chem. 1885, **38**, 1576. Braconnot, Ann. Chim. Phys. 1819, (2), **12**, 185. Blondeau de Carolles, Ann. 1844, **52**, 412; J. prakt. Chem. 1844, **33**, 439. Fehling, Ann. 1845, **53**, 135; Marchand, J. prakt. Chem. 1845, **35**, 200. Bechamp, Ann. 1856, **100**, 364. Allihn, J. prakt. Chem. 1880, **130**, 61.

[1] Ann. 1891, **267**, 341; Ber. 1892, **25**, 322; Zts. ang. Chem. 1892, **5**, 154.

[2] Zts. Zuckerind. 1906, **30**, 270; abst. J. S. C. I. 1906, **25**, 388; J. C. S. 1906, **90**, i, 401; Rep. Chim. 1906, **6**, 404; Ber. 1906, **39**, 1947; Chem. Centr. 1906, **77**, I, 1581; Chem. Ztg. 1906, **30**, 155; Zts. ang. Chem. 1907, **20**, 455; Jahr. Chem. 1905–1908, II, 958. H. Berger and A. Ernest, Ber. 1907, **40**, 4671; abst. Wag. Jahr. 1907, **53**, II, 230. See Stora Kopparbergs Bergslags Aktiebolag, F. P. 402331, 1909; abst. J. S. C. I. 1909, **28**, 1221; Wochenbl. Papierfab. 1909, **40**, 4265; Pap. Ztg. 1909, **43**, 1682.

[3] U. S. P. 970029. E. P. 18341, 1907; abst. J. S. C. I. 1908, **27**, 514; 1910, **29**, 1173; C. A. 1908, **2**, 1642; Chem. Zentr. 1908, **79**, I, 784; Chem. Ztg. Rep. 1908, **32**, 42; Wag. Jahr. 1908, **54**, II, 326; Zts. ang. Chem. 1908, **21**, 1094. F. P. 380358, 1907; abst. J. S. C. I. 1908, **27**, 32. Belg. P. 201746, 1907. U. S. P. 1035086, 1042332, 1046160, 1912; 1050723, 1913; 1087356. 1087743, 1087744, 1914; abst. J. S. C. I. 1912, **31**, 912, 1075; 1913, **32**, 103, 192; 1914, **33**, 349. E. P. 6741, 1910; abst. J. S. C. I. 1911, **30**, 504. F. P. 402331, 1909; abst. J. S. C. I. 1909, **28**, 1221. D. R. P. 193112, 1906; Chem. Zentr. 1908, **79**, I, 784; 1909, I, 1296; Chem. Ztg. Rep. 1908, **32**, 42; Jahr. Chem. 1905–1908, II, 861; 1909, **62**, 344; 1910, **63**, II, 419; Wag. Jahr. 1908, **54**, II, 326; Ztg. ang. Chem. 1908, **21**, 1094. D. R. P. 207354, 1907; Pap. Ztg. 1908, **33**, 386; 1909, **34**, 1682; 1910, **35**, 649, 690, 2519; Chem. Ztg. 1909, **32**, 182; 1910, **34**, 223; Wochenbl. Papierf. 1910, **41**, 638; Pap. Fab. 1910, **8**, 238, 582; Svensk kemisk. Tidskrift 1909, Pt. 7; Zts. Chem. Ind. Koll. 1908, **3**, 47; C. A. 1909, **3**, 2070; Chem. Zentr. 1909, **80**, I, 1296; Wag. Jahr. 1909, II, **55**, 228; Zts. ang. Chem. 1909, **22**, 599.

lyes, he[1] adds a catalyzer to the liquid before fermentation to oxidize the liquor, which is then aerated.

H. Ost[2] and with W. Wilkening[3] first dissolve the cellulose in strong sulfuric acid of 65%–72% strength for a few hours at room temperature to change it into soluble dextrins, which are subsequently converted into dextrose by diluting the mixture with water until it contains 2%–3% H_2SO_4 and 0.2%–0.5% of cellulose and boiling for 5–8 hours; or for 2 hours in an autoclave at 120°. Whereas they compute that theoretically 100 gm. of water-free cellulose gives 111.1 gm. dextrose; in several instances they actually obtained 100 gm. Working along similar lines, only hydrolyzing with dilute sulfuric acid, R. Willstaetter and L. Zechmeister[4] obtained 56%–83%.

Hydrofluoric acid has been employed in the hydrolysis of proteins[5] and cellulose[6] (in the form of filter paper), using a lead vessel to carry out the reaction. It was found that HF up to 30% concentration had but little action, but with acid of 40%–50%

---

[1] Swed. P. 34624, 1912; abst. C. A. 1914, **8**, 1669.

[2] Ber. 1913, **46**, 2995; abst. J. C. S. 1913, **104**, i, 1148; C. A. 1914, **8**, 120; J. S. C. I. 1913, **32**, 822, 1062; Bull. Soc. Chem. 1914, (4), **16**, 95; Chem. Zentr. 1913, **84**, II, 2035; Chem. Ztg. Rep. 1913, **37**, 624. For the utilization of sisal waste in the production of alcohol, see Tropical Life, 1917, **13**, 155; Bull. Agric. Intell. 1918, **9**, 988; J. S. C. I. 1918, **37**, 677-A. Chem. Ztg. 1912, **36**, 1099; abst. J. S. C. I. 1912, **31**, 713, 980; Chem. Ztg. Rep. 1913, **37**, 68. Ann. 1913, **398**, 313; abst. J. S. C. I. 1913, **32**, 784; Bull. Soc. Chim. 1913, (4), **14**, 1262. Willstaetter and Zechmeister, Ber. 1913, **46**, 2401; abst. Bull. Soc. Chim. 1913, (4), **14**, 1354. Ost and Wilkening, Chem. Ztg. 1910, **34**, 461; abst. Chem. Zentr. 1910, **81**, I, 2074.

[3] Chem. Ztg. 1910, **34**, 461; abst. C. A. 1910, **4**, 1888; J. S. C. I. 1910, **29**, 688; J. C. S. 1910, **98**, i, 364; Bull. Soc. Chim. 1911, (4), **10**, 61; Chem. Zentr. 1910, **81**, I, 2074; Jahr. Chem. 1910, **63**, II, 420; Meyer Jahr. Chem. 1910, **20**, 318; Wag. Jahr. 1910, **56**, II, 392; Zts. ang. Chem. 1910, **23**, R, 1534. See also, Flechsig, Zts. Physiol. Chem. 1883, **7**, 913.

[4] Ber. 1913, **46**, 2401; abst. C. A. 1913, **7**, 3413; J. C. S. 1913, **104**, i, 955; J. S. C. I. 1913, **32**, 822; Bull. Soc. Chim. 1913, (4), **14**, 1354. Hydrochloric acid has been patented for purposes of cellulose hydrolysis as far back as D. R. P. 11836, 1880; abst. Wag. Jahr. 1881, **27**, 818.

[5] L. Hugouneng and A. Morel, J. pharm. chim. 1908, **99**, 486; Compt. rend. 1908, **146**, 1291; **147**, 212; 1909, **148**, 236; Bull. Soc. Chim. 1908, (4), **3**, 612, 1146; abst. C. A. 1908, **2**, 2397; 1909, **3**, 662, 1039; J. S. C. I. 1908, **27**, 764; Rev. Chim. 1908, **8**, 409; Chem. Zentr. 1908, **79**, II, 332; Jahr. Chem. 1905–1908, II, 4498, 4501; Meyer Jahr. Chem. 1908, **18**, 236, 239. See also Compt. rend. 1906, **142**, 1426. P. Schuetzenberger, Ann. Chim. Phys. 1879, (5), **16**, 334.

[6] J. Ville and W. Mestrezat, Compt. rend. 1910, **150**, 783; abst. C. A. 1910, **4**, 2094; J. C. S. 1910, **98**, i, 301; J. S. C. I. 1910, **29**, 483; Bull. Soc. Chim. 1910, (4), **7**, 362, 1064; Rep. Chim. 1910, **10**, 281; Chem. Zentr. 1910, **81**, I, 1781; Jahr. Chem. 1910, **63**, II, 419; Meyer Jahr. Chem. 1910, **20**, 253, 318; J. d'Orlowsky, Belg. P. 226890, 1910.

concentration action is more vigorous, and a rapid destruction of the cellulose soon sets in, the mixture assuming a brown color. With 50% acid concentration there is obtained an average of 41 gm. glucose per 100 gm. cellulose, when the process is carried on for 6 hours. They observe on heating glucose with 50% HF that the sugar is gradually destroyed and 53.5% of it disappears when the heating is continued for six hours. This observation may account for the relatively small yield of glucose obtained in the hydrolysis of cellulose as compared with the possible theoretical yield, on the assumption, of course, that the main product of hydrolysis is glucose.

A. Ernest[1] in hydrolyzing various cellulose materials such as ramie and cellulose from sugar beet, found only dextrose in the hydrolyzed product. On the other hand, on the assumption that all the sugar formed is dextrose, the conversion to alcohol in practice is small, and according to E. Hagglund,[2] considerable amounts of pentoses may be found in the final product.

A. Claessen[3] has made an exhaustive technical study of this.

1. Zts. Zuckerind. 1906, **30,** 270; abst. J. S. C. I. 1906, **25,** 388; J. C. S. 1906, **90,** i, 401; Rep. Chim. 1909, **6,** 404; Ber. 1906, **39,** 1947; Chem. Centr. 1906, **77,** I, 1581; Ztg. ang. Chem. 1907, **20,** 455. See also A. Ernest and H. Berger, Ber. 1907, **40,** 4671; abst. Wag. Jahr. 1907, **53,** II, 230.

2. J. prakt. Chem. 1915, **91,** 358; abst. C. A. 1915, **9,** 3127; J. C. S. 1915, **108,** i, 629; J. S. C. I. 1915, **34,** 883; Biol. Chem. Zts. 1915, **69,** 181.

3. U. S. P. 700616, 1902; abst. J. S. C. I. 1902, **21,** 867; Mon. Sci. 1902, **58,** 190. U. S. P. 825808, 1906; abst. J. S. C. I. 1906, **25,** 771; Chem. Zts. 1906, **5,** 495; C. A. 1907, **1,** 116; Mon. Sci. 1907, **67,** 55. U. S. P. 696800, 1902; Re. 12108, 1903; abst. J. C. S. I. 1902, **21,** 630; 1903, **22,** 706; Mon. Sci. 1902, **58,** 190. U. S. P. 654518, 1900; Re. 12069, 1902; abst. J. S. C. I. 1903, **22,** 153; Chem. Ztg. 1900, **24,** 693; Mon. Sci. 1902, **58,** 13. U. S. P. 695795, 1902; abst. J. S. C. I. 1901, **20,** 734; 1902, **21,** 630; Mon. Sci. 1902, **58,** 190. U. S. P. 707903, 1902; abst. J. S. C. I. 1902, **21,** 1190; Mon. Sci. 1903, **59,** 111. U. S. P. 1101061, 1914; abst. J. S. C. I. 1914, **33,** 761. E. P. 258, 259, 1900; abst. J. S. C. I. 1900, **19,** 364, 1028. E. P. 4199, 1901; abst. J. S. C. I. 1901, **20,** 734. E. P. 12588, 1901; abst. J. S. C. I. 1901, **20,** 1008. E. P. 22709, 1905; abst. J. S. C. I. 1906, **25,** 898. F. P. 365595, 1906; abst. C. A. 1907, **1,** 2429; J. S. C. I. 1906, **25,** 1000; Mon. Sci. 1907, **67,** 99. F. P. 295847; abst. J. S. C. I. 1901, **20,** 1008; 1902, **21,** 358; Mon. Sci. 1901, **57,** 41. F. P. 448496, 1912; abst. J. S. C. I. 1913, **32,** 441. D. R. P. 111868, 1899; abst. Wag. Jahr. 1900, II, 288; Chem. Centr. 1900, II, 608; Chem. Ztg. 1900, **24,** 524; Zts. ang. Chem. 1900, **13,** 651; Jahr. Chem. 1900, **53,** 809. D. R. P. 118540, 1900; Wag. Jahr. 1901, II, 280; Chem. Ztg. 1901, **25,** 252; Zts. ang. Chem. 1901, **14,** 348; Jahr. Chem. 1901, **54,** 844. D. R. P. 118542, 1900; Wag. Jahr. 1901, II, 281; Chem. Centr. 1901, I, 716; Chem. Ztg. 1901, **25,** 249; Zts. ang. Chem. 1901, **14,** 348. D. R. P. 118543, 1900; Wag. Jahr. 1901, II, 282; Chem. Centr. 1901, I, 716; Chem. Ztg. 1901, **25,** 249; Zts. ang. Chem. 1901, **14,** 349. D. R. P. 118544, 1900; Wag. Jahr. 1901, II, 282; Chem. Centr. 1901, **72,** I, 716; Chem. Ztg. 1901, **25,** 249; Zts. ang. Chem. 1901, **14,** 349; Jahr. Chem. 1901, **54,** 844. D. R. P. 121869, 1900; Wag. Jahr. 1901, II, 282; Chem. Ztg. 1901, **25,** 571;

problem, employing, in general, sulfur dioxide in the gaseous or liquid state as the hydrolyzing material. He uses also a mixture of 0.2% H_2SO_4 with 20% SO_2 dissolved in water. The reaction is carried out in a current of air and the material heated to a temperature of 120°–145° for one hour at a pressure of 6–7 atmospheres. When this process was attempted on an industrial scale many were the difficulties which were encountered, but it is of particular interest since it was the beginning of this industry in the United States for the production of ethyl alcohol from wood. In 1903 the United States patent rights for the Claessen process were acquired by a firm in Chicago, Illinois, and after experimentally demonstrating this process to its satisfaction, erected a plant at Hattiesburg, Miss. at a cost of about $250,000 to operate on long-leaf pine saw mill waste. This plant was substantially a failure because of the number of mechanical and technical difficulties, the chief of which were as follows:[1] (a) the length of time necessary to hydrolyze the wood was found to be 4–6 hours; (b) the large quantity of acid needed; (c) the action of the acid and water in the rotating digester reduced the wood to a very fine powder, and formed much sulfuric acid which acted upon the sugar and other substances present to form gums and caramels, and so made the complete extraction of the sugar from the residue both unduly tedious and expensive; (d) the digester was lead lined, and the buckling and breaking of the lining necessitated repairs after every two or three "cooks," which proved a great source of delay and expense. A. Claessen[2] found technical difficulties in dealing with cellulose materials containing tannic and gallic acids, such as oak, chestnut, and in a lesser degree the poplar and beech. Gallic acid appears to be always formed on hydrolysis of these woods, which materially interferes during the subsequent fermentation of the sugars. The trouble was finally overcome by the addition

Zts. ang. Chem. 1901, **14**, 788. D. R. P. 123911, 1900; Wag. Jahr. 1901, II, 283; Chem. Centr. 1901, **72**, II, 1032; Chem. Ztg. 1901, **25**, 940; Zts. ang. Chem. 1901, **14**, 1144. D. R. P. 161644; abst. J. S. C. I. 1905, **24**, 1078; Wag. Jahr. 1905, II, 338; Chem. Centr. 1905, **76**, II, 660; Chem. Ztg. 1905, **29**, 772; Zts. ang. Chem. 1905, **18**, 1567. Zts. Verein Zuckerind, 1900, 589; 1901, 348, 351, 754; 1907, **57**, 206, 525; abst. Meyer Jahr. Chem. 1907, **17**, 375, 376. Can. P. 77979, 81207, 84014. Belg. P. 139919, 1898; 142335, 1899.

[1] Chem. Trade J. & Chem. Engr. 1918, **63**, 231.

[2] U. S. P. 825808, 1906; abst. J. S. C. I. 1906, **25**, 771; C. A. 1907, **1**, 16; Mon. Sci. 1907, **67**, 55.

of a ferric salt to the liquid after hydrolysis. In the French modification of the Claessen process,[1] the by-products are said to have value as a cattle food.

M. Ewen and G. Tomlinson[2] who were associated with the Claessen process, began experimenting along new lines in order to remedy the defects of the Hattiesburg plant. Instead of using an aqueous solution of sulfur dioxide, they passed the gas into the digester along with steam, which furnished therefore, both the heat and moisture required. Somewhat later however, Ewen and Tomlinson abandoned the use of SO_2 and were granted a patent[3] covering the use of sulfuric acid as the catalytic agent. This patent and the process patented by E. Simonson[4] disclose a.

---

[1] F. P. 365595, 1906, abst. C. A. 1907, **1,** 2429; J. S. C. I. 1906, **25,** 1000; Mon. Sci. 1909, **67,** 99.

[2] U. S. P. 763472, 1904; abst. J. S. C. I. 1904, **23,** 797. Belg. P. 220462, 1909. F. P. 343006, 1904, abst. J. S. C. I. 1904, **23,** 797, 994. E. P. 30072, 30073, 1912; abst. J. S. C. I. 1914, **33,** 132, 156. U. S. P. 1032440 to 1032450, 1912; abst. J. S. C. I. 1912, **31,** 832, 833. U. S. P. 938308, 1909; abst. Chem. Ztg. Rep. 1909, 659; Zts. ang. Chem. 1909, **22,** 2462; Pap. Ztg. 1910, **35,** 262; J. S. C. I. 1910, **29,** 38; C. A. 1910, **4,** 381. U. S. P. 1032391, 1032392, 1912; abst. J. S. C. I. 1912, **31,** 762, 832; C. A. 1912, **6,** 2863. F. P. 408229, 1909; abst. J. S. C. I. 1910, **29,** 586. G. Tomlinson, "Wood Waste as a Source of Ethyl Alcohol," Chem. and Met. Eng. 1918, **19,** 552; J. S. C. I. 1918, **37,** 711-A; 274-R. Orljavacer Chemische Fabrik, F. P. 357432, 1905; abst. J. S. C. I. 1906, **25,** 117. J. d'Orlowski, F. P. 405187, 1909; abst. J. S. C. I. 1910, **29,** 230. F. P. 343006, 1904; abst. J. S. C. I. 1904, **23,** 994. E. P. 10664, 1904; abst. J. S. C. I. 1905, **24,** 808. R. McKee, U. S. P. 1273392, 1284739, 1284740; 1918; abst. J. S. C. I. 1918, **37,** 600-A; 1919, **38,** 71-A. E. P. 120520, 1918; abst. J. S. C. I. 1918, **37,** 780-A. Paper, 1919, **24,** 584; abst. C. A. 1919, **13,** 1927. E. P. 24589, 1909; abst. J. S. C. I. 1910, **29,** 710. G. Foth (Chem. Ztg. 1913, **37,** 1145, 1221, 1297; Zts. Spirit. Ind. 1913, **36,** 161, 485, 497, 595; Deut. Essigind. **17,** 481; abst. C. A. 1914, **8,** 1343; Chem. Zentr. 1913, **84,** II, 1831; Wag. Jahr. 1913, **59,** II, 431; Zts. ang. Chem. 1913, **26,** I, 519; II, 432), found 0.5% by weight of fusel oil in alcohol by this process, with only traces of methyl alcohol and no acetone. For the preparation of xylose from corn cobs, see C. Hudson and T. Harding, J. Am. Chem. Soc. 1917, **39,** 1038; 1918, **40,** 1601; abst. J. S. C. I. 1917, **36,** 730; 1918, **37,** 778-A. B. LaForge and C. Hudson, J. Ind. Eng. Chem. 1918, **10,** 925; J. S. C. I. 1919, **38,** 86-A. K. Munroe, J. Am. Chem. Soc. 1919, **41,** 1002; abst. J. S. C. I. 1919, **38,** 550-A; C. A. 1919, **13,** 2036. For production of alcohol from peat, refer to G. Pradel, E. P. 5128, 1907; J. S. C. I. 1908, **27,** 416.

[3] U. S. P. 938308, 1909; abst. J. S. C. I. 1910, **29,** 38; Mon. Sci. 1910, **73,** 87. F. P. 408299, 1909; abst. J. S. C. I. 1910, **29,** 586. Can. P. 146794, 1913; abst. C. A. 1913, **7,** 2137.

[4] D. R. P. 92079, 1894; abst. Chem. Centr. 1897, **68,** II, 559; Wag. Jahr. 1897, **43,** 543, 978. In the T. Wagner process (U. S. P. 1261328, 1918; abst. J. S. C. I. 1918, **37,** 410-A,) the fermented sugar-containing liquor resulting from the hydrolysis of cellulosic material is concentrated, after the distillation of the alcohol, the concentrated product containing more than 30% of reducing sugars (calculated as dextrose) and approximately 25%–35% of water.

See R. Ruttan, J. S. C. I. 1909, **28,** 1290; abst. C. A. 1910, **4,** 637; Chem. Zentr. 1910, **81,** I, 1393; Zts. ang. Chem. 1910, **23,** 860; Jahr. Chem. 1909, remarkable identity as to ideas. They erected a plant at Georgetown, South Carolina for the demonstration of their process, which plant was later acquired by a powder company, and has been intermittently operated up to the present time.[1]

On an industrial scale, cellulose in the form of sawdust may be converted first to sugar and finally to alcohol in the following manner. Sawdust from several sawmills is brought by the aid

---

62, 99; Wag. Jahr. 1909, **55,** II, 368; Chem. Ztg. Rep. 1909, **33,** 59. Comp. Industrielle des Alcools de l'Ardeche, F. P. 391057, 1908; E. P. 26619, 1908; abst. J. S. C. I. 1908, **27,** 1126; 1909, **28,** 998. F. P. 358696, 1905; abst. J. S. C. I. 1906, **25,** 277. F. Gallagher and I. Pearl, Eighth Intl. Cong. Appl. Chem. 1912, **13,** 147; J. S. C. I. 1912, **31,** 870. H. Fenton, J. S. C. I. 1901, **20,** 757. J. Teeple, J. Ind. Eng. Chem. 1913, **5,** 680; abst. C. A. 1914, **8,** 1665. R. Hauers and B. Tollens, Ber. 1903, **36,** 3306; abst. Chem. Centr. 1903, **84,** II, 1167; J. C. S. 1904, **86,** i, 16; J. S. C. I. 1903, **22,** 1151; Bull. Soc. Chim. 1904, (3), **32,** 1104; Jahr. Chem. 1903, **56,** 1011. R. Hauers, Dissertation, Gottingen 1902. J. Koenig, D. R. P. 265483; abst. Chem. Zentr. 1913, **84,** II, 1535; Chem. Ztg. Rep. 1913, **37,** 587; Wag. Jahr. 1913, **59,** II, 348; Zts. ang. Chem. 1913, **26,** 653. E. P. 8006, 1914; abst. J. S. C. I. 1915, **34,** 901; C. A. 1916, **10,** 75. V. Omelianski (Compt. rend. 1897, **125,** 1131; Arch. des Sc. biolog. 1900, **7,** 411; Chem. Centr. 1900, **71,** I, 918) in studying the products of the fermentation of cellulose, fermented pure paper in the presence of calcium carbonate at a temperature of about 35° for 13 months. The products obtained from 3.473 gm. of paper were: acetic series of acids, 2.24 gm.; CO_2, 972 gm.; and hydrogen, 0.014 gm. The acids were chiefly acetic and butyric, with small quantities of valeric. Higher alcohols and odoriferous products were also formed but not isolated. No methane was detected.

[1] Several years ago western capital erected a plant at Port Hadlock, Washington, on Puget Sound, for the production of ethyl alcohol and cattle food from sawdust obtained from mills at Seattle, Tacoma, Everett, Anacortes, and Port Blakeley. The plant was equipped with 6 digesters of the same size and type as those that were developed in France by the Compagnie Industrielle des Alcohols de l'Ardeche. These digesters consist of steel cylinders, $2^1/_2$ m. in internal diam. by $2^1/_2$ m. in length, through which are placed 22 tubes, 160 mm. in diam. The outside of each of a tube head has a flanged boiler steel jacket, one to receive the live steam from the boiler and the other to take off the condensed steam, the heating being indirect, the idea being to save steam by means of the indirect heating. Sawdust and enough water are added through a manhole into the space between the tubes to raise the moisture content to about 45%. Anhydrous sulfur dioxide was then added, and the mixture was cooked at 75–100 lbs. pressure. The cost of conversion was excessive because of the very rapid corrosion of the digesters, the long time necessary to heat indirectly, and because the sulfurous acid gas leaked from the digester into the stream space, thereby preventing the use of the low pressure steam. In addition, the extraction equipment was inefficient and out of date, though the buildings of the plant were excellent and expensive, and much of the equipment was imported from France at a large cost.

The extracted sawdust—which had only from 50%–60% of the sugar formed extracted from it—was mixed with Hawaiian molasses, and was put on the market as a cattle food. It was necessary to dry the extracted material down to about 12% moisture in order to prevent decay, and this caused trouble because of explosions of dust in the driers. In addition, the plant was situated about 80 miles from a railway, which greatly increased transportation charges. These facts coupled with the very poor design and equipment—

of belts to a central factory, and is there distributed between several digesters in which the acid hydrolysis is to be carried out. These digesters are of a spherical shape 12 feet in diameter, with steel plate construction and lined with a special acid-resisting brick. After the digester has been charged with sawdust, sulfuric acid is added until the acid constitutes about 0.5% to 1% on the wood, calculating on the dry weight. The vessel is then

especially digester and extraction equipment—were no doubt the prime reasons which caused the failure of this plant.

The alcohol company subsequently disposed of the Georgetown plant, and the company was reorganized, a considerable amount of foreign capital being introduced. A large plant for the production of 5,000 gallons of ethyl alcohol per day was erected at Fullerton. At this plant from 25%–28% of the anhydrous wood is rendered soluble, and of this amount 80% can be converted into fermentable sugar, though to accomplish this requires most careful control. It is likely that a greater percentage will be obtained by the use of dilute acids. For the present, therefore, a conversion yielding 20%–22% of fermentable sugars, or from 10%–11% of ethyl alcohol corresponding to a maximum of, say, 35 gallons of 95% alcohol per dry ton, represents the immediate goal. On a large scale the actual average yields have hardly exceeded half of this amount, so that there is a wide margin for improvement.

An excellent description of the process and of the plant employed is given in a paper on "By-Products of the Lumber Industry," issued by the U. S. Dept. of Commerce, from which the following details are taken. The sawdust is conveyed on a belt from several sawmills to the alcohol plant, and lifted into storage bins by means of an elevator. From the storage bin it is distributed to four digestors as required for charging. These digesters are of spherical shape, 12 ft. in diam. They are of steel-plate construction and are lined with acid proof brick. After a digester is charged with sawdust, diluted sulfuric acid is added until it constitutes about 0.5%–1% of the weight of the dried wood. The digestion is then slowly rotated by means of a worm gear by direct steam. The pressure gradually rises to 120 lbs. and a maximum temperature of 335° F. is reached. The total time of digestion, including charging, heating up, cooking, blow-off, and discharge, is about one hour.

After complete digestion the digester is discharged, and the wood, now known as "hydrolyzed" wood, is carried by belt conveyors to the diffusion batteries, in which the soluble constituents of the mass are extracted with hot water, in the same manner as in tannin-extract manufacture and in sugar extraction. The product of the digester contains more water than the raw material—which often contains 50% water—owing to the addition of the dilute sulfuric acid and to the condensation of steam used for the heating. After extraction the washed residue, consisting of unchanged sawdust, is conveyed to compressors, where the water contained is reduced to about 55%. It is afterwards burnt as fuel, and is sufficient for the generation of all the steam and power required in the plant.

The liquor from the diffusion battery, known as wood liquor, contains sulfuric acid, sugar, and other organic compounds, and is next hydrolyzed with milk of lime in tanks fitted with agitators. It then flows into a storage tank. It is further clarified by decantation, and after cooling is pumped into the fermenting vats. Yeast grown in wood liquor is added, after which fermentation proceeds. The fermented liquor is then distilled in stills for the production of rectified alcohol. The alcohol thus produced is of a high grade, and is reported to contain only traces of fusel oil, esters, and ethers. When properly purified, it differs in no respect from the ordinary grain alcohol.

slowly rotated by means of a worm-gear while steam is used for heating, the maximum temperature reached being 120°. The time of charging, heating up, cooking, blowing off and discharging is about one hour. After the hydrolysis, the acid liquor containing the sugar, is passed through diffusion batteries in order to remove unchanged wood and to separate the soluble portion. The insoluble residue of practically unchanged sawdust is conveyed to hydraulic presses where its water content is reduced to 55% by pressure alone. The mother liquor from the diffusion batteries is neutralized with lime in tanks fitted with stirrers, it is further clarified by decantation and after cooling is pumped into fermentation vessels. Yeast which has grown in wood liquor is added, and the fermentation allowed to proceed. The fermented liquor is finally distilled in column-stills for the production of concentrated alcohol.

A. de Posnansky and L. Spassky[1] first purify their cellulose material before attempting hydrolysis, and extract the material with dilute alkaline solution to remove resins and tannins. Next, in order to remove lignin, they heat with a dilute solution of calcium bisulfite for two hours and follow this by an acid treatment. The purified material is hydrolyzed with a dilute solution of hydrochloric, sulfuric or hydrofluoric acids, saccharification

At the Fullerton plant it was estimated in 1913 that if a monthly capacity of 100,000 gallons had been reached, the cost would not have exceeded 21 cents per gallon, as against 30 cents, the cost of grain alcohol at American distilleries in 1913. But since the summer of 1916 the plant has been running continuously, taking advantage of the high prices ruling.

The quality of the product at Fullerton was reported upon as one of the purest cologne spirits that had come under the observation of the analyst. If the cost of production should be higher than in 1913, then the fact that alcohol from either grain or molasses is more than double the price of that year, would still leave the advantage in favor of the product from wood waste. As the sugars used in wood alcohol can be used for feeding animals, as is done with cane molasses, there would seem to be great possibilities here. In the same paper a short account is also given of the manufacture of alcohol from sulfite liquor, in which similar reactions take place as those already described. This process has been introduced on a large scale in Sweden, and at three paper mills in that country about a million and a quarter gallons of alcohol are obtained per annum from sulfite liquor, and the process is also being worked in the United States.

[1] L. Spassky, F. P. 451268, 1913; abst. J. S. C. I. 1913, **32**, 620; C. A. 1913, **7**, 3187; Mon. Sci. 1914, **81**, 42. A. de Posnansky and L. Spassky, F. P. 459593, 1912; abst. J. S. C. I. 1913, **32**, 1167; C. A. 1914, **8**, 2637. Swiss P. 61410, 1912; 63563, 1913; abst. C. A. 1914, **8**, 2276. A. de Posnansky, F. P. 464502, 468188; 473925, 1913; abst. J. S. C. I. 1914, **33**, 497, 978; 1915, **34**, 729; C. A. 1914, **8**, 3215.

being complete after three hours. The alkaline and bisulfite treatments as well as the acid hydrolysis are all carried out at 140°. The volatile acids present are removed by distillation under reduced pressure, the residual sugar solution being finally neutralized and extracted with alcohol.

F. Gallagher[1] in hydrolyzing sawdust distils off any volatile products present such as turpentine, in the first stages of the heating. He also allows the volatile products formed during the hydrolysis to escape continuously, or intermittently, while maintaining the pressure. He claims to obtain by this procedure a greater yield of sugar and a liquid more suitable for the fermentation process.

The bisulfite treatment referred to above for removal of lignin and other compounds, gives a liquor containing small quantities of sugar. In the preparation of wood pulp for paper manufacture, an enormous quantity of these waste sulfite liquors are formed and many schemes have been suggested for their utilization.[2]

A preliminary treatment of crude cellulose materials by means of chlorine has been suggested.[3] The cellulose, without washing, is digested with 1% of its weight of sulfuric acid for 30 minutes under a pressure of 9 kilograms. It has also been suggested in the case of straw[4] to heat under pressure with water. The solution obtained is employed for the extraction of a second quantity of straw. Each portion is extracted twice under pres-

---

[1] U. S. P. 1056161, 1913; 1091327, 1914; abst. J. S. C. I. 1913, **32,** 441; 1914, **33,** 497. F. Gallagher and H. Mork, U. S. P. 1037185, 1056162, 1056163, 1913. E. P. 400, 14939, 1913; abst. J. S. C. I. 1913, **33,** 441, 1166; 1914, **33,** 801; C. A. 1912, **6,** 3340. F. Gallagher and H. Mork, U. S. P. 1033064, 1912; abst. J. S. C. I. 1912, **31,** 833. E. Gazagne and R. Demuth, F. P. 477077, 1914; abst. J. S. C. I. 1916, **35,** 613.

[2] H. Landmark, Chem. Ztg. 1915, **39,** 98; abst. J. S. C. I. 1915, **34,** 275. A. Frohberg, Wochenbl. Papier-Fabr. 1913, **44,** 4432; abst. J. S. C. I. 1913, **32,** 1152. J. Koenig, J. Hasenbaeumer and M. Braun, Zts. ang. Chem. 1913, **26,** 481; abst. J. S. C. I. 1913, **32,** 939. Holzverkohlungs Industrie A. G. Belg. P. 254945, 256353, 1913.

[3] Standard Alcohol Co. U. S. P. 1032443, 1032444, 1032449, 1032450, 1033064, 1912; 1056162, 1913; 1096030, 1914; abst. Mon. Sci. 1914, **81,** 139. F. P. 452920, 452921, 453129, 460085, 1913; abst. J. S. C. I. 1912, **31,** 833; 1913, **32,** 441, 761, 833; 1914, **33,** 37; C. A. 1914, **8,** 3215. D. R. P. 279991, 1913; abst. C. A. 1915, **9,** 2124. Aust. P. 71273, 1916; abst. C. A. 1916, **10,** 2497. Swed. P. 41072, 1916; abst. C. A. 1916, **10,** 2612. Norw. P. 27188, 1916; abst. C. A. 1916, **10,** 3172.

[4] W. Giles and F. Norris, U. S. P. 918997, 1909; abst. J. S. C. I. 1909, **28,** 538; C. A. 1909, **2,** 1795; Mon. Sci. 1909, **71,** 142.

sure, first with a solution from a previous extraction, and secondly with water. The united solutions are acidified, and when saccharification is complete, are neutralized and fermented.

An important advance was made by R. Willstaetter and L. Zechmeister[1] in 1913. They found that fuming hydrochloric acid of a specific gravity of 1.209–1.212 at 15°C., (containing 41% concentration of acid) was capable of hydrolyzing cellulose in the cold. One part of cellulose in the form of cotton was added to seven parts of concentrated hydrochloric acid. In a very short period the cotton had dissolved. When water was added to the solution after it had stood for a short period, the cellulose was precipitated quantitatively. If however, the concentrated solution of the cellulose be allowed to stand for two days and then diluted, no cellulose is precipitated, but instead an optically active solution is obtained. The solution, moreover, has strong reducing properties when tested with Fehling's solution. It is claimed dextrose is formed to the extent of 95%–96% of the possible theoretical conversion. The concentrated hydrochloric acid solution containing the dissolved cellulose is optically inactive at first, but after an hour, a slight rotation is observable. The rotatory power then gradually increases and becomes constant at the end of 24–48 hours, the actual number of hours depending on the concentration of the hydrochloric acid. The rotation figure does not increase regularly from zero to its maximum, but rises for the first few hours, then remains practically constant for a short period and finally increases again until the maximum is reached. These changes are interpreted on the assumption that an intermediate compound is formed at an early stage during the hydrolysis.

According to these workers, cellulose in other forms such as filter paper, or pine wood, may also be hydrolyzed by very concentrated hydrochloric acid (specific gravity 1.2). In the case of pine wood a 30% residue of lignin substances is obtained. Concentrated hydriodic acid is less reactive, and with the latter heating is necessary in order to dissolve the cellulose. Hydrobromic acid (specific gravity 1.78), concentration (66%), behaves

---

[1] Ber. 1913, **46**, 2401; abst. J. S. C. I. 1913, **32**, 822; J. C. S. 1913, **104**, i, 955; C. A. 1913, **7**, 3413; Bull. Soc. Chim. 1913, (4), **14**, 1354; Chem. Zentr. 1913, **84**, II, 1209.

in a manner similar to hydrochloric acid (41%), the hydrobromic acid dissolving the cellulose even at 0°. With hydrofluoric acid of 70%–75% strength a similar action takes place.

In view of R. Willstaetter and L. Zechmeister's work concerning the action of concentrated hydrochloric acid on cellulose in the cold, it is of interest to refer to H. Fenton's experiments[1] in which he treats cellulose (Swedish filter paper—50 gm.) with dry hydrogen chloride dissolved in an inert solvent (carbon tetrachloride). He obtains 3.1 gm. of chloromethylfurfural and 1.57 gm. of dextrose. According to Fenton the two latter compounds are probably produced in equa-molecular proportions initially, but part of the dextrose formed is destroyed during the heating. Similar reactions take place with hydrogen bromide. The formation of these halogen derivatives point to the presence of a ketohexose nucleus or grouping in the cellulose complex.

R. Willstaetter and L. Zechmeister, in their hydrolysis with concentrated hydrochloric acid, identified their products solely by means of optical activity determinations and copper reduction figures. They did not, however, prove the quantitative yield to dextrose by actual isolation of the dextrose or a derivative of the sugar. H. Ost,[2] regards their results, especially with the higher concentrations of cellulose, as improbable. According to M. Cunningham[3] the products of hydrolysis of cellulose are not identified by the rotation constants of the hydrolyzed solution, and in support of this view adduces the following reasons. Widely different types of cellulose such as cotton and esparto-cellulose give identical optical rotation data on hydrolysis, but the ultimate products necessarily have divergent constituents. In addition, it is known that concentrated hydrochloric acid produces constitutional changes even in the simple hexoses—large fluctuations in optical activity accompanying slight variation in the strength

[1] Proc. Chem. Soc. 1901, **17,** 166; abst. J. S. C. I. 1901, **20,** 757; Chem. News, 1901, **84,** 7; Rep. Chim. 1901, **1,** 515; Chem. Centr. 1901, **72,** II, 405; Chem. Ztg. 1901, **25,** 591; Jahr. Chem. 1901, **54,** 840.

[2] Ber. 1913, **46,** 2995; abst. J. C. S. 1913, **104,** i, 1148; C. A. 1914, **8,** 120; J. S. C. I. 1913, **32,** 1062; Bull. Soc. Chim. 1914, (4), **16,** 95; Chem. Zentr. 1913, **84,** II, 2035; Chem. Ztg. Rep. 1913, **37,** 624. Chem. Ztg. 1912, **36,** 1099; abst. J. S. C. I. 1912, **31,** 713, 980; Ann. 1913, **398,** 313; J. S. C. I. 1913, **32,** 784.

[3] J. C. S. 1918, **113,** 173; abst. C. A. 1918, **12,** 1379; J. S. C. I. 1918, **37,** 236-A; Ann. Rep. Soc. Chem. Ind. 1918, **3,** 127, 149.

of acid. Cellulose under the action of concentrated hydrochloric acid forms esters of polysaccharoses containing acidic hydroxyl groups. Cunningham failed to isolate dextrose from the solution.

F. Gallagher and I. Pearl[1] have made a series of experiments on the hydrolysis of sawdust from long-leaf pine wood screened through a 10-mesh sieve. The proportion of sulfuric acid used was 1 per cent. of the dry weight of wood, the proportion of liquor was 3:1, the maximum pressure was 135 lb. per sq. in., maintained for 30 minutes, and the total duration of the treatment was about 70 minutes. The digested material was extracted with water, evaporated to a density of 1.045 and fermented. Subsequent hydrolysis of the residue gave a further yield of fermentable sugars. The following table illustrates some of the results obtained:

TABLE VII.—HYDROLYSIS OF PINE WOOD

Material	Total Extract	Reducing Material	Fermentable Sugars	Ratio of Fermentable Sugars to total Extract	Cellulose	
					Before Digestion	After Digestion
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
a. Long leaf pine sawdust...	22.0	19.3	11.8	0.53	54.0	52.0
b. Residue from (a)........	6.3	4.7	3.0	0.47	52.0	42.0
c. Residue from (b)........	2.8	1.7	1.6	0.57	..	..
d. Bleached cotton.........	3.1	1.6	1.4	0.44	..	..
e. Residue from (d)........	4.5	2.8	2.5	0.55	..	..
f. Bleached soda wood pulp.	17.7	16.0	6.3	0.36	..	..
g. Residue from (f)........	7.5	4.3	3.8	0.51	..	..

Other investigators who have contributed to this subject include Mitscherlich,[2] Neumann,[3] Voerkelius,[4] G. Foth,[5] R. v.

---

[1] Eighth Intl. Cong. Appl. Chem. 1912, **13**, 147; abst. J. S. C. I. 1912, **31**, 870, C. A. 1912, **6**, 3013.

[2] D. R. P. 72161; abst. Mon. Sci. 1905, **63**, 823; Ber. 1894, **27**, 149; Wag. Jahr. 1893, **39**, 1063; Zts. ang. Chem. 1893, **6**, 732. U. S. P. 284319, 1883.

[3] "Critical Study of the Hydrolysis of Cellulose from Wood." Diss. Dresden, 1910.

[4] Wochenbl. Papierfabr. 1911, **42**, 854; abst. C. A. 1911, **5**, 2942; Chem. Ztg. Rep. 1911, **35**, 852.

[5] Chem. Ztg. 1913, **37**, 1145, 1221, 1297; abst. C. A. 1914, **8**, 1343; Chem. Zentr. 1913, **84**, II, 1831; Wag. Jahr. 1913, **59**, II, 431; Zts. ang. Chem. 1913, **26**, I, 519; II, 432; Zts. Spirit. Ind. 1913, **36**, 161, 485, 497, 595; Deut. Essigind. **17**, 481.

Demuth,[1] C. Schwalbe and W. Schulz,[2] Societe anonyme "Origo",[3] H. Wallin,[4] W. Cohoe,[5] T. Koerner,[6] F. Zimmer,[7] H. Ruediger,[8] W. Gentzen and L. Roth,[9] and G. Zemplen.[10]

Patent protection for carrying these ideas into effect, have been granted to E. Bouchard-Praceiq,[11] A. Boernen,[12] H. Bergstrom,[13] E. Tillberg,[14] and others.[15]

Cellulose Hydrates. Alkali Cellulose. The action of alkalis on cellulose is much different from that of acids. Whereas the milder alkalis such as soap, borax, and sodium phosphate have no action upon cellulose, nor has ammonia under ordinary circum-

---

[1] Zts. ang. Chem. 1913, **16**, 786; abst. C. A. 1914, **8**, 1343; Chem. Zentr. 1914, **85**, I, 924; Wag. Jahr. 1913, **59**, II, 432.

[2] Ber. 1910, **43**, 916; abst. J. C. S. 1910, **98**, i, 301; C. A. 1910, **4**, 1751; J. S. C. I. 1910, **29**, 688; Chem. Zentr. 1910, **81**, I, 1781; Jahr. Chem. 1910, **63**, II, 419; Meyer Jahr. Chem. 1910, **20**, 253; Zts. ang. Chem. 1910, **23**, 1244.

[3] D. R. P. 204058; abst. J. S. C. I. 1909, **28**, 35; Chem. Zentr. 1908, **79**, II, 1900; Chem. Ztg. Rep. 1908, **32**, 671; Jahr. Chem. 1905–1908, II, 179; Wag. Jahr. 1908, **54**, II, 327; C. A. 1909, **3**, 686.

[4] Swed. P. 26825, 1907; Norw. P. 18687, 1908; Chem. Ztg. Rep. 1919, 251; Pap. Fab. 1910, **8**, 311; Pap. Ztg. 1910, **35**, 569, 649, 690, 1110, 1387, 2118.

[5] J. S. C. I. 1912, **31**, 513; abst. C. A. 1912, **6**, 3329; Chem. Zentr. 1912, **83**, II, 1074; Chem. Ztg. Rep. 1912, **36**, 485.

[6] Zts. ang. Chem. 1908, **21**, 2353; Sci. Amer. 1909, **67**, 238; Pap. Ztg. 1908, **33**, 3707; C. A. 1909, **3**, 484; J. S. C. I. 1908, **27**, 1216; Bull. Soc. Chim. 1908, (4), **6**, 230; Mon. Sci. 1909, **70**, 326; Chem. Zentr. 1908, **79**, II, 2049; Chem. Ztg. Rep. 1909, **32**, 692; Jahr. Chem. 1905–1908, II, 179; Meyer Jahr. Chem. 1908, **18**, 392; Wag. Jahr. 1909, **54**, II, 339.

[7] Mitteil. d. landw. Inst. kgl. Univ. Breslau, 1902, **2**, 245.

[8] Chem. Ind. 1905, **28**, 547; abst. Chem. Centr. 1905, **76**, II, 1697.

[9] D. R. P. 147844, 1901; abst. Mon. Sci. 1905, **63**, 71; 1909, **71**, 327; Chem. Centr. 1904, **75**, I, 410; Chem. Ztg. 1904, **28**, 66; Jahr. Chem. 1904, **57**, 878; Wag. Jahr. 1904, **50**, II, 370; Zts. ang. Chem. 1903, **16**, 244.

[10] "Sugar and Alcohol from Wood," Budapest, 1910.

[11] F. P. 393336; abst. J. S. C. I. 1909, **28**, 103; Meyer Jahr. Chem. 1909, **19**, 420; Zts. Spiritsind. **32**, 237.

[12] Zts. ang. Chem. 1908, **21**, 2355; E. P. 16262, 1904; abst. J. S. C. I. 1905, **24**, 808; Chem. Ztg. 1905, **29**, 1234; Chem. Zts. 1905, **4**, 354.

[13] Pap. Fabr. 1909, **7**, 506, 507, 1314; 1910, **8**, 506; 1912, **10**, 677; Svensk Papperstidning, 1904, Pt. 10, 116.

[14] Swed. P. 25283, 1907. See Segerfelt, Svensk Kemisk Tidskrift, 1911, 149. Hofer, Allg. Fischereiztg. 1906, **31**, No. 4.

[15] Stova Kopparbergs Bergslags, Aust. P. 41479, 1909. See also, Stutzer, Pap. Ztg. 1910, **35**, 3930. Klason, Pap. Fabr. 1909, **7**, 27; Tek. Tidskr. Afd. Kemioch Bergsvetenskap, 1893, 49; 1908, Pt. 7. Willstaetter, Ber. 1913, **46**, 2401; Klein, Pap. Fabr. 1914, **12**, 630. Mattheus, Pap. Fabr. 1910, **8**, 532. Krause, Chem. Ind. 1906, **29**, 217; Pap. Ztg. 1907, **32**, 1100. Key-Aberg, Svensk Papperstidning, 1914, 45. Tomlinson, Chem. Ztg. Rep. 1909, 659. Ost, Chem. Ztg. 1910, **34**, 461. Krause, Chem. Ind. 1903, **29**, 217. Hoenig, Pap. Fabr. 1912, **10**, 103. Akt. Ges. "Ethyl," Swed. P. 34624, 1912.

stances, L. Vignon has pointed out,[1] that if cotton is heated under pressure with concentrated aqueous ammonia, or with ammonia combined with calcium chloride, a nitrogenous compound is obtained if the temperature is raised to 200°, while the cellulose—unchanged in external appearance—behaves toward acid dyes like the animal fibers.

On the other hand, dilute alkaline hydroxides or lime do not adversely effect the fiber, if during the operation air be rigidly excluded. In the presence of air, however, and at high temperatures, oxycellulose readily forms, with consequent tendering of the fiber. Non-recognition of this fact is apt to give rise to difficulties in bleaching, and care therefore must be exercised in boiling cotton with lime or alkali under pressure, to ensure the substantial absence of air or other sources of oxygen. At the ordinary temperature cellulose appears to be adversely effected by caustic soda, the oxidation appearing to increase with increase in concentration of the alkali.

With alkaline hydroxides of high concentration, cellulose undergoes both a physical and chemical change, a fact observed as far back as 1844 by J. Mercer, a calico printer of Lancashire, England, and to him science is chiefly indebted for the first clear statement of the observable phenomenon which occurs when cotton cellulose is treated with concentrated alkaline hydroxides, sulfuric acid or zinc chloride.[2] Mercer followed up the subject only

---

[1] Compt. rend. 1891, **112**, 487, 623; abst. Chem. News, 1891, **63**, 153, 285; J. C. S. 1891, **60**, 662; J. S. C. I. 1891, **10**, 694; Bull. Soc. Chim. 1891, **5**, 472, 474, 557; Mon. Sci. 1891, **37**, 415, 533; Ber. 1891, **24**, R, 259; Chem. Centr. 1891, **62**, I, 683, 898; Chem. Tech. Rep. 1891, **30**, I, 38; Chem. Ztg. Rep. 1891, **15**, 76, 111; Jahr. Chem. 1891, **44**, 2814, 2824; Wag. Jahr. 1891, **37**, 1124; Deut. Chem. Ztg. 1891, 109; Centr. Textilind. 1891, 90; Indbl. 1891, 109. L. Vignon and L. Cassela & Co., D. R. P. 57846; abst. Chem. Centr. 1892, **63**, I, 80; Chem. Ind. 1891, **14**, 560; Chem. Tech. Rep. 1891, **30**, II, 119; Wag. Jahr. 1891, **37**, 1121; Zts. ang. Chem. 1891, **4**, 560; Indbl. 1891, 382; Tech. Chem. Jahr. 1891–1892, **14**, 485. French Patent. 206007, 1890; abst. Mon. Sci. 1891, **37**, 229; D. R. P. Anm. C-3408, abst. Mon. Sci. 1891, **38**, 1003.

[2] The discovery was apparently the outcome of an experiment carried out by Mercer in connection with his investigations of the theory of solution, his object being to induce a partial separation of different hydrates of caustic soda by filtering its solution through cotton. For this purpose a filter composed of six folds of cotton was made, but a solution of caustic soda poured into the filter was found to pass through very slowly and to lose in strength as the result of the act of filtration. At the same time the cotton cloth used as a filter was found to have undergone an extraordinary change, having become translucent, contracted in both dimensions, and thickened.

intermittently, and it was not until six years later that he embodied his ideas in patent form.[1] After demonstrating that upon treatment of cotton with strong caustic soda solution, the cellulose swelled up, shrunk greatly, and became more transparent, he endeavored to more closely examine the phenomenon by measuring the density of the alkali before and after it had been in contact with the cellulose, and found that it decreased from 1.30 to 1.25. As the result of his investigations it was found that (a) sulfuric acid and zinc chloride acted similarly under certain conditions, while (b) warming the alkali solution retarded the action, and cooling accelerated it. Best results were obtained by Mercer when working with sodium hydroxide solutions of 20°-30° Bé. density the firmness of the threads increasing in the ratio of 13 to 22. It was also found that the action of the alkali upon the cellulose increases proportionately with the concentration of the NaOH.

Mercer came to the conclusion that a definite compound results from the action of concentrated alkali upon cellulose, and that the compound formed is represented by the formula $C_{12}H_{20}O_{10}.Na_2O$, which is, in turn, decomposed by water into a hydrated cellulose $C_{12}H_{20}O_{10}.H_2O$ and NaOH. This latter formula nearly corresponds to the increase in weight (4.5%-5.5%) of the cotton after treatment. He considered that at 100° this water of hydration is liberated along with the hygroscopic moisture, but is reabsorbed when the fabric is again exposed to the air. He was also aware of two other changes brought about by this alkaline treatment, i. e., the greater tensile strength of the treated fabric, and secondly a considerable increase in affinity for coloring matters, especially the organic dyestuffs.

J. Gladstone next investigated the change in the minute structure of the cotton cell when induced by treatment with alkali[2]

[1] E. P. 13296, 1850; Dingl. Poly. 1850, **121**, 438; 1851, **122**, 318; Jahr. Chem. 1851, **4**, 747; Rep. Patent Invent. 1851, 358; Practical Mech. Jour. 1851, 115; Deutsche Muster Ztg. 1851, I. No. 6.

For German claim to priority of discovery of the action of alkali on cellulose, see Polytechnische Ztg. published by Leuchs & Co. Jan. 28, 1847.

[2] J. C. S. 1853, **5**, 17; Phil. Mag. 1853, **5**, 313; Chem. Gaz. 1852; Dingl. Poly. 1852, **124**, 158; J. prakt. Chem. 1852, **56**, 247; Jahr. Chem. 1852, **5**, 823. See also W. Grüne, Must. Ztg. 1851; abst. Poly. Notizbl. 1852, **7**, 20. Varrentrap, Poly. Notizbl. 1853, **8**, 268.

Gladstone's method of examination consisted in immersing 20 gm. hanks of cotton in caustic soda solutions of various concentrations, expressing the alkali, and repeatedly washing the cellulose with alcohol to remove the while W. Crum[1] extracted with alcohol cotton which had been treated with strong caustic potash, in order to remove the excess of reagent. The fiber thus extracted gave up to water the whole of the potash in combination, which was determined and found to agree with the formula $(C_6H_{10}O_5)_2KOH$—that is, it contained but half as much alkali as Mercer's product. This formula, has since been the subject of much criticism. However, Crum and Gladstone together established that with solutions of sodium hydroxide of strengths exceeding 10% of NaOH when brought in contact with cellulose at ordinary temperatures, changes were induced as above indicated, and as the result of a definite reaction (under identical concentration and temperature conditions), and that this compound of cellulose and alkali is not firmly fixed, as is seen by the fact that decomposition results even upon washing with cold water, the alkali remaining unchanged, and the cellulose going to a hydrated form. Upon treatment with alcohol instead of water, but half of the alkali is liberated.

In 1901 E. Thiele published his investigations, and in the main, corrobrated the composition of alkali-cellulose as determined by Mercer and Gladstone, and further showed that in the inter-

---

NaOH. After vacuum drying the amount of soda retained was estimated either by noting the increase in weight of the cotton, or by washing out the soda with water and determination of the alkalinity. From the results of these experiments he concluded "it appears that lignine is capable of forming a combination with soda, the proportion of the alkali varying with the strength of the solution employed, but in no instance exceeding one atom, and this compound is decomposed by water, being resolved into its original compounds."

[1] J. C. S. 1863, **16**, 1, 404; Man. Lit. Phil. Soc. 1863–1864, **6**, 186; abst. Chem. News, 1862, **5**, 319; Chem. Centr. 1863, **34**, 927; 1864, **35**, 238; Chem. Tech. Rep. 1863, **2**, II, 25; Jahr. Chem. 1863, **16**, 782; Wag. Jahr. 1863, **9**, 615.

Crum examined cotton fiber before and after mercerization, and found that the action of the alkali was to cause the flattened fiber to assume the round, solid form of ripe cotton. While at the same time the central opening is decreased in size, if not completely obliterated. He considered the contraction of the mercerized fibers to be due to the twisting of the fiber under the influence of the alkali, and is increased by mercerizing, so that there is consequent shortening of it sufficient to account for the shrinking in length and breadth, and the thickening of any fabric submitted to the process. Diagonal lines were sometimes observed in the ripe, treated fibers giving the impression of a spiral structure, but these evidently are due to the creasing or corrugating effect of extreme twisting.

C. O'Neill (Text. Col. 1876, **1**, 325) carried on experiments with twenty individual New Orleans cotton filaments, and measured the contraction in length and the increase of strength of each filament after treatment with caustic soda of sp. gr. 1.250. The contraction amounted to 139/996 or about 15%, and the strength increased from 138 to 154 grains, or nearly 12%.

action of the latter with carbon bisulfide whereby viscose is formed, the alkali-cellulose appears to play the rôle of an alkali alcoholate.[1] He described a cellulose hydrate obtained with concentrated aqueous ammonia, which is distinguished from the other cellulose hydrates in possessing a greater elasticity and resiliency.

The next year[2] appeared the patented process of the Vereinigte Kunstseidefabriken for producing stable alkaline solutions of cellulose hydrate by dissolving the hydrate in a 3%–40% (some range) solution of NaOH. This firm proposed to impregnate cotton goods with cellulose hydrate which are then passed through a weak acid bath whereby the cellulose hydrate is precipitated upon and between the fibers of the fabric, forming, after washing, a solid, lustrous finish.

C. Cross and E. Bevan had previously made the observation[3] that the hydrated modification of cellulose affords a ready means for preparing the cellulose benzoates. By treatment of the alkaline solution with benzoyl chloride,[4] these derivatives may readily be formed, and are soluble in glacial acetic acid, from which solu-

---

[1] Zts. Farb. Text. Chem. 1902, 73; Chem. Ztg. 1901, **25,** 610; abst. J. C. S. 1901, **80,** i, 634; J. S. C. I. 1901, **20,** 890; Chem. Centr. 1901, **72,** II, 405; Jahr. Chem. 1901, **54,** 889; Meyer Jahr. Chem. 1901, **11,** 446; Wag. Jahr. 1901, **47,** II, 514. See also E. Thiele, U. S. P. 710819, 1902; abst. J. S. C. I. 1902, **21,** 1393. U. S. P. 750502, 1904. E. P. 8083, 1902; abst. J. S. C. I. 1903, **22,** 550. D. R. P. 133427; abst. Chem. Ztg. 1902, **26,** 971; Chem. Zts. 1903, **2,** 438; Wag. Jahr. 1902, **48,** II, 469. D. R. P. 134312; abst. Mon. Sci. 1904, **61,** 104; Chem. Ztg. 1902, **26,** 852; Chem. Zts. 1903, **2,** 438; Jahr. Chem. 1902, **55,** 1053; Wag. Jahr. 1902, **48,** II, 470. D. R. P. 154507; abst. Chem. Centr. 1904, **75,** II, 1179; Chem. Ztg. 1904, **28,** 962; Chem. Zts. 1905, **4,** 534, 540; Jahr. Chem. 1905–1908, II, 988; 1910, **63,** II, 427; Wag. Jahr. 1904, **50,** II, 391; Zts. ang. Chem. 1904, **17,** 1864. D. R. P. 157157; abst. Chem. Centr. 1905, **76,** I, 576; Chem. Ztg. 1905, **29,** 11; Chem. Zts. 1905, **4,** 540; Jahr. Chem. 1905–1908, II, 987, 988; 1910, **63,** II, 427; Wag. Jahr. 1904, **50,** II, 392; Zts. ang. Chem. 1905, **18,** 434. Belg. P. 162701, 171980. F. P. 320446. Aust. P. 21119.

[2] E. P. 17501, 1902; abst. J. S. C. I. 1903, **22,** 817. F. P. 323475; abst. J. S. C. I. 1903, **22,** 508; Mon. Sci. 1903, **59,** 128. D. R. P. 155744; abst. Chem. Centr. 1904, **75,** II, 1678; Chem. Ztg. 1904, **28,** 1113; Chem. Zts. 1905, **4,** 249; Wag. Jahr. 1904, **50,** II, 385; Zts. ang. Chem. 1905, **18,** 197.

[3] Chem. News, 1890, **61,** 87; abst. Chem. Centr. 1890, **61,** I, 584; Chem. Ztg. Rep. 1890, **14,** 58. Chem. Ztg. 1909, **33,** 368; abst. C. A. 1909, **3,** 1589; J. C. S. 1909, **96,** i, 290; Bull. Soc. Chim. 1909, **6,** 985; Chem. Zentr. 1909, **80,** I, 1471. H. Ost. and F. Westhof, Chem. Ztg. 1909, **33,** 197; abst. C. A. 1909, **3,** 1394; J. S. C. I. 1909, **28,** 325; J. C. S. 1909, **96,** i, 210; Zts. ang. Chem. 1909, **22,** 1856; Chem. Zentr. 1909, **80,** I, 1231; Jahr. Chem. 1909, **62,** II, 385; Rep. Chim. 1909, **9,** 321; Bull. Soc. Chim. 1909, **6,** 685; Wag. Jahr. 1909, **55,** II, 514.

[4] Ber. 1886, **19,** 3218; abst. J. C. S. 1887, **52,** 228; Bull. Soc. Chim. 1887, **47,** 427; Jahr. Chem. 1886, **39,** 1426.

tions they may be recovered by precipitation with water. It was pointed out that a noteworthy property of these hydrated celluloses is that they are assimilable by microscopic organisms, i. e., that they form an excellent nidus for moulds.

In order to shed further light upon the subject of the combination of cellulose with alkali, W. Vieweg[1] immersed purified cotton dried at 90°, in caustic soda of varying strengths. After the cellulose had stood in contact with the NaOH for two hour periods, the alkali was titrated, and from the diminution in the strength of the latter, the amount of alkali entering into combination with the cellulose was calculated. The amounts found to have been taken up are shown in the following table:

TABLE XIX.—ACTION OF CAUSTIC SODA ON CELLULOSE

Concentration: Gm. NaOH in 100 cc. Lye	Gm. NaOH taken up by 100 Gm. Cellulose
0.4	0.4
2.0	0.9
4.0	2.7
8.0	4.4
12.0	8.4
16.0	12.6
20.0	13.0
24.0	13.0
28.0	15.4
33.0	20.4
35.0	22.6
40.0	22.5

According to Vieweg therefore, the absorption of caustic soda rises rapidly until the concentration of the lye reaches 16%, when the absorption remains constant up to a strength of lye of 24%. It then rises and becomes constant again at 35% strength. The amount of caustic soda taken up from the 16% lye is about 13%, and this figure corresponds to the compound $(C_6H_{10}O_5)_2NaOH$ isolated by Gladstone by extracting cotton,

---

[1] Papier Ztg. 1907, **32**, 130, 174; 1908, **34**, 149; Ber. 1907, **40**, 3876; 1908, **41**, 3269; abst. C. A. 1907, **1**, 1320; 1908, **2**, 3403; J. C. S. 1907, **92**, i, 893; 1908, **94**, i, 857; J. S. C. I. 1907, **26**, 836, 1157; 1908, **27**, 1081; Bull. Soc. Chim. 1908, **4**, 902; Rep. Chim. 1908, **8**, 62; Chem. Zentr. 1907, **78**, II, 1780; 1908, **79**, II, 1584; Chem. Ztg. Rep. 1908, **32**, 27, 619; Meyer Jahr. Chem. 1907, **17**, 215; 1908, **18**, 506; Ztg. ang. Chem. 1908, **21**, 1184; Wochenbl. Papierfabr. 1907, **38**, 1890. See also W. Herbig, Zts. Text. Ind. 1900–1901, **4**, 785; abst. Chem. Centr. 1901, **72**, II, 1115; Jahr. Chem. 1901, **54**, 890. See W. Vieweg, D. R. Anm. 7215, 1907.

which had been steeped in strong caustic soda, with alcohol. On the other hand, the amount of caustic soda taken up from a lye exceeding 35% in strength would correspond about to an alkali cellulose having the composition $(C_6H_{10}O_5)_2(NaOH)_2$. From the results thus obtained it is certain that in mercerizing, chemical action takes place, for an adsorption or a distribution of caustic soda between water and cellulose would not take place in molecular proportions in such widely different concentrations (16%–24%, 35%–40%).

The author further points out that cellulose which has been treated with caustic soda solutions beyond a certain strength has acquired after washing in water, then in acetic acid and again in water, the property of absorbing more caustic soda from a dilute solution of the latter than the same cotton untreated.

Vieweg found[1] that from 11%–24% solutions of sodium hydroxide, cellulose takes up an amount of alkali sufficient to form the compound $C_{12}H_{19}O_{10}Na$, and if the results are plotted the curve obtained is discontinuous, the point of discontinuity corresponding with the formation of this compound. He has also shown that the higher the degree of mercerization the greater the capacity for absorption of sodium hydroxide, more being taken up at lower than at higher temperatures.

The views of Vieweg are not shared by O. Miller who has been unable to substantiate Gladstone's formula for mercerized cellulose,[2] in that he finds the percentage of sodium hydroxide in mercerized cellulose increases with the concentration of the alkaline solution. He has shown[3] that if cellulose is dried for six hours at 95°, treatment with concentrated sodium hydroxide solution at 10° indicates practically no alteration in weight. As the result of criticisms recently made by C. Cross[4] and

---

[1] Ber. 1908, **41**, 3269; abst. J. S. C. I. 1908, **27**, 1081.

[2] Ber. 1907, **40**, 4903; 1908, **41**, 4297; abst. J. S. C. I. 1909, **28**, 37; Chem. Zentr. 1908, **79**, I, 453; 1909, **80**, I, 273; J. C. S. 1909, **96**, i, 13; 1908, **94**, i, 78; J. Russ. phys. Chem. Soc. 1905, **37**, 361; Bull. Soc. Chim. 1907, **2**, 141; Chem. Ztg. Rep. 1908, **32**, 82; Jahr. Chem. 1905–1908, II, 962; Meyer Jahr. Chem. 1908, **18**, 506; Wag. Jahr. 1907, **53**, II, 507.

[3] Ber. 1910, **43**, 3430; abst. C. A. 1911, **5**, 1187; J. C. S. 1911, **100**, i, 17; J. S. C. I. 1911, **30**, 18; J. Soc. Dyers Col. 1911, **27**, 10; Bull. Soc. Chim. 1911, **10**, 1150; Rep. Chim. 1911, **11**, 178; Chem. Zentr. 1911, **82**, I, 355; Chem. Ztg. Rep. 1911, **35**, 35.

[4] Ber. 1911, **44**, 153; abst. C. A. 1911, **5**, 1513; J. C. S. 1911, **100**, i, 114; Bull. Soc. Chim. 1911, **10**, 1297; Rep. Chim. 1911, **11**, 232; Chem. Zentr.

C. Schwalbe,[5] upon the accuracy of the investigations of Miller, he

1911, **80,** I, 519; Kunst. 1912, **2,** 14; J. S. C. I. 1911, **30,** 204.

[5] Ber. 1911, **44,** 151; abst. C. A. 1911, **5,** 1513; J. C. S. 1911, **100,** i, 114; Bull. Soc. Chim. 1911, **10,** 1297; J. S. C. I. 1911, **30,** 204; Rep. Chim. 1911, **11,** 232; Chem. Zentr. 1911, **80,** I, 519; Kunst. 1912, **2,** 14. C. Schwalbe, (Zts. Chem. Ind. Koll. 1908, **2,** 229; abst. J. S. C. I. 1908, **27,** 278; Chem. Zentr. 1908, **79,** I, 1216; Chem. Ztg. Rep. 1908, **32,** 204; Zts. ang. Chem. 1908, **21,** 1377) records a case in which cotton cloth was beaten in a papermaker's beater for several hours until it was converted into a gelatinous cellulose hydrate. When this was dyed with Benzopurpurin 10B it was colored a bluish black instead of the normal red color of the dyestuff. Congo Red and Benzopurpurin 4B, on the other hand, did not show the blackening. The abnormal reaction was finally traced to the presence of colloidal copper in the pulp, derived from the bronze knives of the beater. Benzopurpurin 10B is sensitive to copper and forms a blue copper compound.

As C. Schwalbe has pointed out (Zts. ang. Chem. 1909, **22,** 197; abst. J. S. C. I. 1909, **28,** 216; C. A. 1909, **3,** 1143; Bull. Soc. Chim. 1909, **6,** 552; Rep. Chim. 1909, **9,** 490; Chem. Zentr. 1909, **80,** I, 840; Chem. Ztg. Rep. 1909, **33,** 120; Jahr. Chem. 1909, **62,** II, 385; Wag. Jahr. 1909, **55,** II, 514) it is necessary to emphasize the difference between hydrolysis and hydration in the case of cellulose, although under certain conditions both may occur simultaneously. The hydrocelluloses, products of hydrolytic action, are generally characterized by free carbonyl groups which reduce Fehling's solution. The cellulose hydrates may be produced, with or without simultaneous hydrolysis, whenever cellulose is subjected to the action of alkalis, acids, or salts which exert a swelling or solvent influence in presence of water. According to Cross, hydration may take place in presence of water by mechanical action alone. Besides the cellulose hydrates artificially produced from the normal cellulose (anhydride), other types exist in nature which have never attained the dehydrated and polymerized condition of a normal cellulose. These undeveloped types are sometimes included in the group of "hemicelluloses." The hydrated celluloses differ widely in their properties, but a high hygroscopic moisture is common to all; the hydrocelluloses on the other hand are distinguished by an abnormally low moisture-content. Some of the hydrates, *e. g.*, mercerized cotton, possess high tensile qualities, others, *e. g.*, the artificial silks, are mechanically deficient. These two groups also differ widely as regards their solubility in alkalis. Under certain conditions, the hydrated celluloses are resistant to esterifying influences to which the normal cellulose responds. All the hydrated celluloses are characterized by a diminished resistance to hydrolysis by acids, to an extent proportional to their "degree of hydration." Many methods have been proposed for the determination of the "degree of hydration" of a given cellulose: Vieweg measures the absorption affinity towards sodium hydroxide, Cross and Bevan utilize the thio-carbonate reaction and measure the viscosity of the product, Hübner uses a colorimetric method with solutions of zinc chloride of different strengths, while Knecht measures the absorption of benzopurpurin under standard conditions. All these methods are open to objections, and the author has devized a method based on the increased susceptibility to hydrolysis by acids. The procedure is as follows: The "copper value" (cupric-reducing value) of the sample is first determined on 3 gm. of the substance in the manner previously described (see J. S. C. I. 1907, **26,** 548). Another portion of the finely chopped substance is then boiled with a standard quantity of sulfuric acid of 5 per cent. strength, for 15 minutes with constant stirring. The acid is neutralized and the prescribed quantity of Fehling's solution is added without separating the hydrolyzed fiber from the liquid. In this way a second "copper value" is obtained, and the difference between the two measures the hydrolysis which has taken place and which is proportional to the "degree of hydration" of the original cellulose.

has gone over his work again,[1] and made further determinations in which precautions were taken to recover any cellulose lost in the lye. The results calculated on dry weights were: mercerized product, 99.6%; fibers, etc. recovered from the alkali after neutralization, 0.26%; loss, 0.14% of the original cellulose taken.

Whereas Vieweg has shown that in mercerization the adsorption is greater, the greater the alkali concentration, J. Briggs[2] points out that an increased adsorption capacity is characteristic of

Some of the more typical results are indicated in the following table.

TABLE XX.—ACTION OF ALKALI ON CELLULOSE

	Hygroscopic Moisture	Copper Value after Hydrolysis	Copper Value before Hydrolysis	Difference
	Per cent.			
Cotton wool	6.1	3.3	1.1	2.2
Ditto mercerized with 8 per cent. soda lye	7.7	3.2	0.9	2.3
Ditto mercerized with 16 per cent. soda lye	10.7	5.0	1.3	3.7
Ditto mercerized with 24 per cent. soda lye	11.3	6.1	1.2	4.9
Ditto mercerized with 40 per cent. soda lye	12.1	6.6	1.9	4.7
"Glanzstoff" silk	9.8	12.8	1.5	11.3
Viscose silk A	10.7	14.0	1.9	12.1
Viscose silk B	10.2	14.5	3.0	11.5
Viscose silk C	11.0	16.6	2.9	13.7
Chardonnet silk	11.4	17.7	4.1	13.6
Girard's hydrocellulose	3.6	6.6	5.7	0.9
Mitscherlich wood pulp, unbleached	....	4.4	2.4	0.9
Ritter-Kellner wood pulp unbleached	....	3.5	2.8	2.7

In their investigations on mercerized cellulose, A. Fraenkel and P. Friedlaender (Mitt. k.k. Tech. Gew. Mus. 1898, 326) found the luster effects are not obtained unless the action of water is associated. Their results showed that using a cotton with a breaking strain of 358 gm. and an elasticity of 21 mm. elongation, mercerization with caustic soda of 35° Bé. gave an average breaking strain of 548 gm. and an elongation of 40 mm. Where cold 10% alcoholic soda was used, the breaking strain registered 618 gm. and elongation 28 mm., whereas when the alcoholic soda was hot, the figures obtained were 720 gm. and 33 mm. respectively.

[1] Ber. 1911, **44**, 728; abst. C. A. 1911, **5**, 2175; J. C. S. 1911, **100**, i, 355; J. S. C. I. 1911, **30**, 413; Bull. Soc. Chim. 1911, **10**, 1297; Rep. Chim. 1911, **11**, 323; Chem. Zentr. 1911, **82**, I, 1164; Kunst. 1912, **2**, 14.

[2] Chem. Ztg. 1910, **34**, 455; Zts. Chem. Ind. Koll. 1911, **8**, 57; abst. C. A. 1910, **4**, 2372; J. S. C. I. 1910, **29**, 622; Bull. Soc. Chim. 1911, **10**, 60; Chem. Zentr. 1910, **81**, I, 2075; Jahr. Chem. 1910, **63**, II, 422; Zts. ang. Chem. 1910, **23**, 1389.

hydrated celluloses generally, by whatever method the hydration may have been induced, and that the increase in adsorption may, in strictly comparative cases, be taken as a measure of the "degree of hydration." He also shows that small differences in the degree of hydration may be measured on a magnified scale by determining the adsorption of the alkali in alcoholic media, instead of in aqueous solutions. The percentage of sodium hydroxide adsorbed by cellulose from 2 per cent. solutions is very much greater in alcoholic media, and it increases with the alcoholic strength. The author finds that maximum adsorption of 14–15 per cent. of sodium hydroxide, calculated on the dry weight of the cellulose, are recorded in the case of artificial silks in presence of 93 per cent. alcohol of approximately $N/2$ alkalimetric strength. By working in 93 per cent. alcohol, it is possible to show differences in the degree of hydration of cellulose fibers which have been hydrated by mechanical means only in the papermaker's beating engine.

H. Wichelhaus and W. Vieweg[1] hold the view that in mercerized cellulose only the cuticle of the fiber is removed[2] is incorrect. By comparing the esters of nitric and benzoic acids derived from natural and mercerized cellulose the change is shown to be chemical in character. The yield of benzoate obtained from 100 parts of cellulose by the action of benzoyl chloride and NaOH,[3] is given as follows:

TABLE XXI.—BENZOYLATION OF CELLULOSE

	Yield, before Mercerizing	Yield, after Mercerizing
Cotton	112	139
Flax	121	137

Again, although the percentage of nitrogen in the nitrates

---

[1] Ber. 1907, **40**, 441; abst. C. A. 1907, **1**, 1266, 1621; J. C. S. 1907, **92**, i, 186; J. S. C. I. 1907, **26**, 195; Rep. Chim. 1907, **7**, 179; Biochem. Centr. 1907, **6**, 90; Chem. Zentr. 1907, **78**, I, 800; Chem. Ztg. Rep. 1907, **31**, 186; Jahr. Chem. 1905–1908, II, 962; Meyer Jahr. Chem. 1907, **17**, 215; Wag. Jahr. 1907, **53**, II, 411; Ztg. ang. Chem. 1907, **20**, 1537.

[2] A. Fraenkel and P. Friedlaender, Mitt. K. K. Tech. Gewerbemus, 1898, 326; abst. J. S. C. I. 1898, **17**, 839; Chem. Centr. 1899, **70**, I, 191; Chem. Ztg. 1898, **22**, 670; Jahr. Chem. 1899, **52**, 1298; Meyer Jahr. Chem. 1898, **8**, 484.

[3] C. Cross and E. Bevan, Chem. News, 1890, **61**, 87; abst. Chem. Centr. 1890, **61**, I, 584; Chem. Ztg. Rep. 1890, **14**, 58. Chem. Ztg. 1909, **33**, 368; abst. C. A. 1909, **3**, 1589; J. C. S. 1909, **96**, i, 290; Bull. Soc. Chim. 1909, **6**, 985; Chem. Centr. 1909, **80**, I, 1471.

derived from cotton and from flax both before and after mercerization is practically constant (13%), the products obtained are different in that the nitrate from the mercerized product gives a much higher solubility in ether-alcohol, a statement which repeatedly has been proven.

C. Beadle and H. Stevens[1] have conducted an investigation as to the influence of temperature on the absorption of water and sodium hydroxide from aqueous NaOH solutions containing from 1% to 25% NaOH using regenerated cellulose, the particular form employed being a monofil of 360 denier made by the cuprammonium process. It was found that for any given temperature between 5° and 40° a maximum hydration takes place, these maxima being greater the lower the temperature; the maxima for 0° however, falls below that for 5°. Similarly, with regard to the absorption of NaOH, in which case maximum absorption at 5°, 12°, 20°, 30° and 40° takes place in 9%, 11%-12%, 12%-14%, and 14% NaOH respectively, the maximum amounts of NaOH absorbed being 256, 162, 112, 82, and 78 parts respectively per 100 parts regenerated cellulose.

According to a recent process,[2] cotton textile or spinners' raw cotton materials are treated with caustic alkali of strength below that which produces the effects of mercerization, whereby the material is improved in elasticity and extensibility. A suitable caustic lye may contain 9% caustic soda but the strength may be varied somewhat and the treatment carried out between 15° and 50°.

E. Heberlein claims[3] that transparent effects on cotton fabrics are produced by subjecting the goods to the action of a caustic alkali solution of at least 15° Bé. (sp. gr. 1.109), washing and then treating with sulfuric acid of at least 50.5° Bé. (sp. gr. 1.498), both treatments being carried out at a temperature below 0°. The order of the treatments may be reversed, and the two treatments may be repeated alternately; one of the reagents may be caused to react only in places to produce pattern effects, and

---

[1] Eighth Intl. Cong. Appl. Chem. 1912, **13**, 25; abst. C. A. 1912, **6**, 3013; J. C. S. 1912, **102**, i, 947; Chem. Ztg. 1912, **36**, 1222.

[2] Fine Cotton Spinners' and Doublers' Assoc., M. Cunningham and C. Cross, E. P. 131212, 1918; abst. J. S. C. I. 1919, **38**, 759-A.

[3] E. Heberlein, U. S. P. 1265082, 1918; abst. J. S. C. I. 1918, **37**, 461-A; C. A. 1918, **12**, 1703; Ann. Rep. Soc. Chem. Ind. 1918, **3**, 159.

the fabrics may preferably be treated under considerable tension.

L. Vignon,[1] E. Grandmougin,[2] R. Wolffenstein and G. Bumcke[3] are among others who have studied this subject, but there are many important points yet to be cleared up before our knowledge in this field may be regarded as satisfactory.

Mercerization. After Mercer secured patent protection in England in 1850,[4] apparently little was done towards its commer-

---

[1] Compt. rend. 1900, **131**, 708; Bull. Soc. Chim. 1901, **25**, 137; abst. Chem. News, 1900, **82**, 255; J. C. S. 1901, **80**, i, 16; J. S. C. I. 1900, **19**, 1103; Mon. Sci. 1900, **55**, 835; Rep. Chim. 1901, **1**, 130; Chem. Centr. 1900, **71**, II, 1151; Chem. Ztg. 1900, **24**, 999; Jahr. Chem. 1900, **53**, 840.

[2] Chem. Ztg. 1908, **32**, 241; abst. Chem. Zentr. 1908, **79**, I, 167; Jahr. Chem. 1905–1908, II, 959. Compare K. Haupt, Faerb. Ztg. **25**, 173. F. Thies, Faerb. Ztg. **25**, 196; Chem. Zentr. 1914, **85**, II, 824.

[3] Ber. 1901, **34**, 2415; abst. J. C. S. 1901, **80**, i, 582; J. S. C. I. 1901, **20**, 925; Bull. Soc. Chim. 1902, **28**, 368; Rep. Chim. 1902, **2**, 46; Chem. Centr. 1901, **72**, II, 529; Jahr. Chem. 1901, **54**, 888.

For the separation of cellulose and its derivatives, the following scheme has been suggested:

A. Celluloses.
B. Hydrated celluloses (Hydrocellulose).
  (a) reducing (hydral-cellulose).
  (b) reducing and with carbonyl groups.
  (c) with carbonyl groups (acid cellulose), and not reducing.
  (d) not reducing, and without carbonyl groups (lactone form).

F. Seibert and J. Minor (Paper, 1919, **24**, 1007; abst. C. A. 1919, **13**, 2440; J. S. C. I 1919, **38**, 713-A) record that in the course of the prolonged beating of unbleached sulfite pulp chemical changes occur which are shown by a progressive increase in the "copper value" of the pulp. This increase is attributed to hydrolysis and oxidation of the cellulose owing to the hydration of the fiber and its prolonged exposure to the air, and does not take place to the same extent when the fiber is rapidly cut up, for instance, in a Jordan refiner. A break in the regularity of the increase in the copper value is noted immediately after the addition of a basic dyestuff, at which point a sharp fall in the copper value takes place, but the loss is again made up by further changes occurring during the subsequent beating. The influence of basic dyestuffs is accounted for by their chemical reaction with the lignin. During the process of washing after bleaching there is a progressive decrease of the copper value, showing that the removal of soluble oxidizable products by washing takes place more rapidly than the formation of such products due to the beating; when washing is stopped the copper value begins to increase. The copper value increases considerably during the process of bleaching, but the increase does not correspond with the quantity of bleach liquor until a large excess of bleach liquor has been used. The loss of weight of the pulp apparently varies directly with the amount of bleach liquor used, but it is not excessive even when the proportion of bleach liquor is high. A distinct advantage in the quality and feel of the paper is derived from the use of a substantial amount of bleach liquor and the loss of strength of the paper is barely appreciable. On the other hand with a large excess of bleach liquor, sufficient to increase the copper value of the pulp to an abnormal extent, especially if kept warm, the destruction of the fibers is very pronounced.

[4] E. P. 13296, 1850; Dingl. Poly. 1851, **121**, 438; Jahr. Chem. 1851, **4**, 747; Rep. Patent Invent. 1851, 358; Practical Mech. Jour. 1851, 115.

cial exploitation. It is recorded, however, that a French concern offered Mercer the sum of two hundred thousand dollars for the purchase of his patent rights which in those days was an immense sum of money. If this be true, it is indicative of the importance which at that time was attached to his discovery. In spite of the many advantages of this process, it has attained a firm industrial footing in the textile trade only within recent years, due primarily to the surface contraction which was then considered inevitable, and which materially increased the cost of the product. Mercers patent was followed by those of J. Mayer-Rauschenbach,[1] J. Sachs,[2] C. Lightoller and J. Longshaw,[3] E. Fremy and A. Urbain,[4] W. Lukacs,[5] and the P. and C. Depoully patents issued in 1883.[6] In the years 1894,[7] 1895,[8] 1896,[9] 1897,[10] 1898,[11] as well as

---

[1] E. P. 340, 1867.

[2] E. P. 2966, 1880.

[3] E. P. 5713, 1881.

[4] E. P. 1816, 1882.

[5] E. P. 3103, 1883.

[6] E. P. 28696, 1883; 8642, 1884; 15140, 1885; 5533, 1895. D. R. P. 30966, 1884; 37658, 1885. See also E. P. 5838, 1884, A. Prinz and E. Quellmalz.

[7] W. Kay and Thornliebank Co. E. P. 19388, 20308, 1894. Compare also E. Goodwin, E. P. 22566, 1892; 16698, 1893.

[8] G. Ormondroyd, E. P. 20785, 1895.

[9] E. P. 8235, 1896; J. Weiss. E. P. 16840, 1896; D. R. P 128284, 1896, F. Bernhardt. E. P. 19428, 1896; D. R. Anm. 12196, 1896; D. R. P. 134449, 1897, J. Schneider. E. P. 19633, 21253, 21942, 1896, A. Liebmann. E. P. 23741, 1896, A. Liebmann and W. Kerr. E. P. 28499, 1896, A Green. E. P. 28870, 1896; D. R. P. 112773, 1896; 133456, J. Bemberg. D. R. P. 120576, 1896, G. Dietrich and O. Seyfert. E. P. 29504, 1896, Salis, Schwade and Co. and A. Bins and R. Boral. E. P. 29832, 1896, Farbwerke vorm. Meister, Lucius & Brüning. D. R. P. 109607, 1896, F. Sheuclen.

[10] E. P. 3218, 1897; F. P. 269138, 1897, A. Bonbon. E. P. 5350, 1897; D. R. P. 98182, 1897; 113458, 1899; 118429, 1900; F. P. 264396, 1897. U. S. P. 679425, 1900, M. Beck. E. P. 5573, 27020, 1897; D. R. P. 99337, 1896, F. Bayer & Co. E. P. 6122, 1897, W. Kay, and Thornliebank Co. E. P. 7093, 1897; D. R. P. 102672, 1896, Kleinewefers Sohne. E. P. 9056, 1897, E. Crepy. F. P. 265009, 1897, Compagnie parisienne des couleurs d'aniline. D. R. P. 109937, 1897; F. P. 269550, 1897, Soc. F. Vanoutryve & Co. E. P. 10784, 11313, 1897, Meister, Lucius, & Brüning. E. P. 15169, 16746, 1897, M. Sharp. F. P. 269380, 1897, A. and H. Pinel. E. P. 17397, 1897, H. Lowe. F. P. 267459, 1897, Dollfus, Mieg. & Co. E. P. 23268, 1897, G. Douglas. E. P. 25948, 1897, J. Hill. E. P. 26247, 1897; D. R. P. 100796, 1897; F. P. 270437, 271509, 1897; 276526, 1898, H. David. D. R. P. 95482, 1897, P. Dosne. D. R. Anm. 5109, 1897; F. P. 263912, 1897, Kahnert. E. P. 27435, 1897, J. Dean, J. Knowles and H. Barker. E. P. 29613, 1897; D. R. P. 102103, 1897; U. S. P. 610619, 1898; F. P. 272994; Swiss P. 14961, 1897, A. Wyser, E. P. 30142, 1897; U. S. P. 646787, W. and H. Aykroyd. U. S. P. 612189, 1897, A. Birch. U. S. P. 608194, 1897, J. Greenwood. D. R. Anm. 9620, 1897; 10798, 1898; D. R. P. 120344, 1898; F. P. 268971, 1897; 424247, 1911, E. Friedrich. D. R. P. 95904, 1897; 100701; F. Mommer & Co. D. R. P. 98968, 1897, U. Ungnad.

[11] E. P. 526, 1898, F. Cloth. E. P. 1839, 1898, G. Oldham. E. P.

1899,[1] 1900,[2] especially in the latter year, and the early part of

2307, 1898, H. Lowe. E. P. 2915, 1898, G. Douglas. E. P. 4067, 4556, 1898, G. Hamilton. E. P. 7317, 1898; D. R. P. 109285, 1899, A. Ashworth. E. P. 7687, 1898, H. Gassner. E. P. 7688, 1898; D. R. P. 109431, 141623, T. Schiefner. E. P. 9885, 1898, J. Hope. E. P. 10246, 1898; D. R. P. 100796, 1897; 107378, 1898; U. S. P. 618399, 1898; F. P. 276941, 1898; H. David. E. P. 10708, 10709, 1898; D. R. P. 177241, 1903, W. Hall. E. P. 10943, 1898, J. and G. Lord. E. P. 12379, 1898; D. R. P. 103328, 1898; 118270, 118271, 1900; 120602, 1899; F. P. 290498, 1899; B. Cohnen. E. P. 12669, 1898, L. Van Westrum. E. P. 13953, 1898, P. Marshall. E. P. 13495, 1898, D. Horsburgh. E. P. 14472, 1898, Cassela & Co. D. R. P. 40506, 156402, 196741; D. R. Anm. 51392, 1910, C. Haubold. E. P. 14917, 1898, J. Nelson. E. P. 16823, 1898, J. Kleinewefers Sohne. E. P. 22101, 1898; D. R. P. 108653, 1898, W. and H. Aykroyd. E. P. 23135, 1898, T. and W. Caldwell, and E. Johnstone. U. S. P. 616709, 1898; Re. 9885, 1898; D. R. P. 106596, 118061, 1898, N. Istomin. E. P. 23325, 1898, B. Ermen. D. R. P. 101813, 108107, 109431, 1898, T. Schiefner and Getzner, Mutter & Co. E. P. 24433, 1898, F. Davis and A. Liebmann. D. R. P. 107379, 108766, 108881, 1898, H. Krissmanech & F. Auderieth. E. P. 24784, 1898, J. Wood. D. R. P. 114192, 1898; F. P. 264546, 1897; 277031, 1898, Soc. Anon. Blanchiment, Teinture et Impression. E. P. 25881, 1898, F. Gros and P. Bourcart. U. S. P. 643781, 1898, R. Subrenat. E. P. 26728, 1898, B. Cohnen. D. R. P. 111370, 1898, J. Ashton and E. Kayser. E. P. 27361, 1898, W. Kay and the Thornliebank Co. D. R. P. 116029, 1898, C. Gadd. U. S. P. 607150, 1898, C. Wichelt and A. Jones.

[1] E. P. 54, 1899, H. Aykroyd. E. P. 859, 1899; D. R. P. 102017, 1897; 109756, 1898, T. Schiefner. E. P. 1079, 1899, S. Schwabe & Co. and Boral, Robin and Kymer. E. P. 2211, 1899, F. Holland and J. Jackson. E. P. 2708, 1899, H. Newell. E. P. 3914, 1899, S. Wood and Park House Dyeing Co. E. P. 4170, 4773, 1899, T. Pickles. E. P. 5469, 1899; D. R. P. 110633, 117249, 1899, Badische Anilin u. Soda Fab. E. P. 5703, 1899, C. Fischer. E. P. 6249, 1899, G. Tagliani. E. P. 6769, 1899, G. Kershaw and A. Seeley. E. P. 9452, 1899; 20519, 1906; U. S. P. 628669, 1898, A. Miller. E. P. 9937, 24163, 1899, J. Copley. E. P. 10936, 1899; U. S. P. 656319, 1899; J. Copley, P. Marshall and R. Heaton. E. P. 11509, 1899; U. S. P. 634362, 1899; F. P. 287998, 1899, P. Marshall. E. P. 10943, 1899; U. S. P. 648275, 1899; F. P. 297067, 1900; D. R. P. 119331, 1899, J. Lord. E. P. 13514, 17642, 1899, G. Grandage. E. P. 14032, 1899, B. Cohnen. E. P. 14329, 1899, P. Jeanmaire. F. P. 287793, 1899, W. Neuhoff. E. P. 14932, 1899, E. Brown. E. P. 15397, 1899, T. Robinson. E. P. 16782, 1899; D. R. P. 106593, 1897; 127161, 1899; A. Römer and E. Hölken. E. P. 18260, 1899, E. Bronnert. E. P. 19936, 1899, R. Brandts. E. P. 20011, 1899, F. Gärtner. E. P. 21162, 1899, A. Boyeux. E. P. 21192, 1899, F. Cochrane. E. P. 21488, 1899; U. S. P. 645698, 1899, L. Weldon. E. P. 22095, 1899, D. Crowther. E. P. 22292, 1899, A. Wyser. E. P. 23098, 1899; D. R. P. 110508, 1898, W. Herschmann. E. P. 23695, 1899, E. Price. E. P. 24188, 1899; U. S. P. 608033, 1897, J. Ecob. E. P. 9521, 19273, 24397, 1899; 2699, 12327, 12580, 1900; F. P. 287924, 1899; 307800, 312957, 1901; D. R. Anm. 21633, 1909, J. Dolder. E. P. 25638, 1899; F. P. 295677, 1899, E. Simon. E. P. 25703, 1899, M. Sharp. U. S. P. 648115, 1899, G. Remsen. U. S. P. 650442, 1899, F. Stelter. U. S. P. 655546, 1899, W. Denn. U. S. P. 617561, 1897; 786264, 1899, H. Butterworth. D. R. P. 113704, 113457, 113374, 1899; F. P. 306197, 1900, Andernacher Textilwerk. D. R. P. 119149, 1899, J. Belger. D. R. P. 112916, 1899, E. Kruse.

[2] E. P. 156, 1900, J. Empsell and E. Firth. E. P. 459, 1900, R. Brandts. E. P. 1577, 1900, O. Isherwood. E. P. 1736, 1900; U. S. P. 657705, 1900, W. Macconnel. E. P. 2699, 11436, 12327, 12580, 1900, J. Dolder. E. P. 3416, 1900, H. Kearns. E. P. 3466, 1900, R. Turner. E. P. 5409, 1900, C. Jack-

1901,[1] 1902[2] and 1903[3] progress in the art was especially rapid.

A silky luster resembling that imparted by mercerization may be given to cotton cloth by means of what is known as a calender finish, the method being called the "Schreiner finish." This is accomplished by passing the cloth between rollers under heavy pressure, one of the rollers being engraved with obliquely set lines ruled from 125 to 600 to the lineal inch. The effect is to produce a great number of parallel flat surfaces on the cloth, which causes it to acquire a high luster. By previously heating the rollers, the finish may be

---

son. E. P. 7189, 1900; D. R. P. 112741, 1899; 119137, 1900; F. P. 290665, 1899; U. S. P. 734333, 1900, P. Jeanmaire. E. P. 8230, 1900, F. Hasslacher. E. P. 8654, 1900; D. R. P. 122750, 1900; F. P. 300601, 1900, O. Kopp and E. Usuelli. E. P. 9505, 1900, J. Ross and J. Schneider. E. P. 11077, 1900; W. Crompton and W. Horrocks. D. R. P. 131134, 131228, 1900, E. Schaeffler. D. R. P. 122488, 1900, F. Klein. D. R. P. 123445, 1900; F. P. 316963, 1901; 401004, 1909, R. Hahn. E. P. 12454, 1900, C. Lavel. E. P. 12550, 1900; H. Brassard. D. R. P. 120302, 1900, A. Schmidt. D. R. P. 119737, 1900, F. Deissler. E. P. 14283, 1900; F. P. 302887, 1900; U. S. P. 682494, 1900; F. Reichmann and C. Lagerquist. D. R. P. 118359, 119427, 1900, Esser and Scheider. E. P. 15329, 1900, J. Obermaier. D. R. P. 122863, 1900, C. Schulze. E. P. 16161, 1900, F. Johnson. E. P. 19937, 1900; D. R. P. 131704, 135695, 1900; 134968, 1901; U. S. P. 661649, 1900; F. P. 305139, 1900, F. Shuman. E. P. 20136, 1900; U. S. P. 657293, 1900, J. Morgan and W. Menzies. E. P. 20377, 1900, F. Gilli. E. P. 21397, 1900, F. Simons. E. P. 23470, 1900; D. R. P. 158272, 1900; F. P. 300693, 1900, M. Frings. U. S. P. 659721, 1900; 685889, 722064, 1901, C. Weichelt. D. R. P. 119333, 1900, A. Kunow. D. R. P. 117255, 1900; D. R. P. 102548, 1897; O. Hoffmann. F. P. 305662, 1900, F. Simons. F. P. 267079, 1900, F. Reichmann. F. P. 305237, 1900, J. Decock.

[1] E. P. 1374, 1901; D. R. P. 119736, 123822, 1900; F. P. 301640, 301641, 1900; U. S. P. 755765, 1902, P. Hahn. E. P. 2697, 1901, J. Dolber. E. P. 3568, 1901, F. Shuman. E. P. 5655, 1901, F. Konitzer. E. P. 6644, 1901, Badische Anilin u. Soda Fab. E. P. 7480, 1901, K. Weldon. E. P. 8076, 1901, A. Hill. E. P. 12476, 1901; 25445, 1906, T. Pickles. E. P. 17735, 1901, J. Gebauer. E. P. 18728, 1901, C. Reichenbach. E. P. 19555, 1901; F. P. 306826, 1901. U. S. P. 694109, 1901. D. R. P. 143612, 1901, A. Römer. E. P. 20394, 1901, J. Pearsons. E. P. 21645, 1901, P. Bourcart. E. P. 22996, 1901, Pearson. E. P. 19089, 23181, 1901. U. S. P. 750694, 1903. D. R. P. 152337, 1903, T. Pratt. D. R. P. 129974, 1901, P. Schmidt and E. Price. D. R. P. 144428, 1901; M. Sarfet. D. R. P. 141132, 1901; F. P. 308117, 1901, J. Ecob. F. P. 309244, 1901, Buffaud and Robatel.

[2] E. P. 2202, 1902, J. Pearson. E. P. 2524, 1902, J. Schneider. E. P. 3376, 1902, G. Mueller. E. P. 5931, 1902, T. French. E. P. 6894, 1902, J. Dutton. E. P. 13217, 1902, J. Spenle. E. P. 13982, 1902, Lang, Bridge & Wood. E. P. 14675, 1902, J. Klauder. E. P. 14525, 1902, Calico Printers Assoc. E. P. 19734, 1902, E. Scott. E. P. 24302, 1902, W. Knowles. E. P. 25163, 1902, J. Nasmith. E. P. 20672, 1902; F. P. 324848, 1902, R. Chevolleau. F. P. 322028, 1902, Beltzer and Thiebaut. F. P. 324076, 1902, L. Brettonniere.

[3] E. P. 894, 1903, P. Edlich. E. P. 5249, 1903, J. Spenle. E. P. 10255, 1903; U. S. P. 680131, 1901; D. R. P. 128647, 1900; 166807, 1904; W. Crompton and W. Horrocks. E. P. 20959, 1903, T. de Naeyer. E. P. 9683, 1903; D. R. P. 157323, 1903; F. P. 333078, 1903, L. Cippolina. E. P. 7872, 1903; D. R. P. 127002, 1900; F. P. 331012, 1900, C. Jackson and E. Hunt. D. R. P. 156434, 1903, E. Kruse. D. R. P. 149140, 1903, H. Gordon. D. R. P. 156402, 1903; 196741, 205962, 212900, 1907; C. Haubold.

For the effect of traces of iron in mercerized cotton, see L. Lefevre and E. Blondel, Rev. mat. Color. 1909, **13**, 313; abst. C. A. 1910, **4**, 386; Chem. Ztg. Rep. 1909, **33**, 597. K. Haertling, Koll, Zts. 1919, **25**, 74.

H. Lowe made a distinct advance in mercerization,[1] and followed this up in 1900[2] with basic improvements.

He clearly showed that in mercerizing cotton piece goods under tension, in addition to obtaining the recognized advantages of mercerizing (increased strength and affinity for coloring matters), that the tension imparted a permanent luster to the goods. This discovery of Lowe did not receive the financial support which its intrinsic value merited, and meeting with no encouragement he allowed his patent rights to elapse. In the interem, R. Thomas and E. Prevost,[3] who had been working along similar lines with Egyptian cotton, and apparently oblivious to the previous work of Lowe—also recognized that a permanent luster was obtainable and took out patents in various countries.[4]

As soon as this product had been placed upon the market wide-spread interest was aroused, and a demand created which has not abated but increased to the present day. For some time mercerization was confined to yarn, but afterwards it was recognized that piece goods could also be satisfactorily treated. Litigation upon the validity of the Thomas and Prevost patents was carried to adjudication in several countries, and were annuled on the grounds of prior disclosure in Lowe's patent specification, and this adversely effected the patents issued after 1889, many of which were allowed to lapse.[5]

The temperature at which mercerization should be carried on is a question of considerable moment, Mercer recommending 16° as the best temperature for conducting the process. Rise in temperature during alkaline impregnation is deleterious to the result, while material reduction in temperature is apt to impart a harsh feel to the finished goods. With lower temperatures

---

made permanent and quite simulate mercerized cotton. See L. Schreiner, E. P. 7637, 1895; 3113, 6315, 1899; 2157, 1900; D. R. P. 113343, 112076, 1899. S. Jones, U. S. P. 1316958, 1919; J. S. C. I. 1919, **38**, 897-A.

[1] E. P. 20314, 1889; 4452, 1890; 17397, 1897; 2307, 1898.

[2] E. P. 4452, 1900. J. Weiss, U. S. P. 586750, 1897.

[3] R. Thomas and E. Prevost, E. P. 18040, 1895; 20714, 1896; 9517, 14201, 1897. D. R. P. 85564, 1895; 97664, 1898, addn. to D. R. P. 85564, 129883, 1900; F. P. 259625, 1896.

[4] The E. Heberlein patents are, E. P. 27529, 1898; 4528, 1907; E. P. 4683, 1909. See also, Heberlein & Co., E. P. 108671, 1917; abst. J. S. C. I. 1918, **37**, 297-A. U. S. P. 624800, 1899.

[5] E. P. 4452, 1890; 18040, 1895; 20714, 1896; 9517, 14201, 1897. D. R. P. 85565, 1895; 97664. D. R. Anm. 21427, 1898; 44213, 1908. F. P. 168742; 246244, 1895; 399904, 1909. A. Hawley, P. Crossland, F. Dixon, E. P. 132647, 133441, 1918,

mercerization may be carried on with less concentrated alkaline solutions. Thomas and Prevost patented the application of artificially cooled caustic soda for this purpose,[1] maintaining that the process may be carried on economically and efficiently with caustic soda of 15°–18° Tw. At the present time, however, refrigeration is seldom employed except to regulate the rise of temperature of the caustic soda when acting upon the cellulose.

Mention is made in the specification of Mercer and elsewhere in literature as to other efficient agents sulfuric acid,[2] caustic potash, zinc chloride,[3] etc.[4] for producing this result, but they have little or no interest from a commercial point of view in this connection.

The time required for mercerization has been recognized from the first as being of very short duration—in fact may be measured by seconds. E. Knecht[5] carried out some interesting experiments with American cotton yarn to shed light on this point, the skeins after immersion being immediately neutralized and then dyed in 1% Benzopurpurin, the results obtained being indicated in the following table.

TABLE XXII.—MERCERIZATION OF COTTON

Immersion Time in Alkali	Shrinkage Per cent.	Amount Dyestuff Taken Up Per cent.
5	15.7	3.24
10	17.4	3.62
20	25.0	3.80
40	25.0	3.89
60	25.0	3.91
180	27.4	4.10

As will be observed, the above figures indicate the major portion of the reaction takes place during the first five seconds.

A permanent luster may be obtained on cotton by various means without tension, but none of the processes have as yet been

---

[1] E. P. 9517, 1897.

[2] M. Rauschenbach, E. P. 340, 1867. C. Brodbeck, E. P. 18119, 1890. K. Schreiner and K Grunert, D. R. P. 312087, 1916.

[3] E. Bronnert, E. P. 18260, 1899.

[4] J. Schneider, E. P. 19428, 1896, used sodium and potassium sulfides. W. Hall, E. P. 10708, 1898, used both alkali and acids. For mercerizing and bleaching simultaneously, see J. Copley, E. P. 24163, 1899.

[5] J. Soc. Dyers Col. 1908, **24**, 68, 112; Chem. Ztg. 1908, **32**, 272; Ztg. ang. Chem. 1909, **22**, 243, 249; Lehne Faerb. Ztg. 1908, 276.

commerialized. Meister, Lucius and Bruening[1] add a strong solution of sodium silicate to the alkali, while Bayer and Co.[2] add a half volume of glycerol to one of caustic soda. The mercerization of loose cotton[3] entails too much waste to make it a paying proposition although many processes[4] have been devised for this purpose. G. Tagliani[5] mercerizes cotton piece goods on one side only by padding the side of the fabric with strong caustic soda by means of an engraved steel cylinder,[6] but the process is restricted to printed goods.

H. Lange,[7] E. Hanausek,[8] J. Huebner alone,[9] and with Pope[10] and F. Teltscher[11] as well as others have sought the cause of the increased luster of cotton mercerized under tension,[12] but there is much lack of harmony in their results.

"When viewed under the microscope in reflected light the irregular surface of the cotton fiber is seen at the points at which the light is reflected, to exhibit a strong luster, and the same holds good for cotton which has been mercerized without tension.

---

[1] E. P. 10784, 11313, 1897. D. R. P. 78601, 1897. D. R. P. 97664, 1898; Chem. Centr. 1898, **69**, II, 1110. D. R. P. 103041, 1896; Chem. Centr. 1899, **70**, II, 550.

[2] E. P. 27020, 1897.

[3] Lowe, E. P. 17397, 1897.

[4] Gros and Boucart, D. R. P. 124135, 1898; F. P. 283587, 1898; U. S. P. 677450, 1899. H. Brassard, D. R. P. 124856, 1900; U. S. P. 670098, 1901. J. Schmidt, D. R. P. 138893, 1901. C. Reichenbach, D. R. P. 129843, 1901; E. P. 18728, 1901. P. Boucart, D. R. P. 145582, 1901; E. P. 21645, 1901. T. Schiefner, D. R. P. 141623, 1901. J. Kleinewefers Sohne, D. R. P. 181927, 1905; F. P. 403724, 1909. E. Steiner, F. P. 364965, 1906. Heberlein & Co., D. R. P. 214512, 1907; E. P. 4528, 1907; F. P. 375068, 1907. C. Ahnert, D. R. P. 209428, 1907; 225704, 1909. J. Copley, E. P. 12551, 1910. J. Robson, U. S. P. 975074, 1910.

[5] E. P. 6249, 1899; D. R. P. 107916, 1897; F. P. 287814, 1899.

[6] For hydrolyzing cellulosic materials, see Testrup and Wet Carbonizing, Ltd. E. P. Appl. 19389, 1918. For hydrated cellulose, see J. DeCew, Belg. P. 256401, 1913; U. S. P. 1140799, 1915; abst. J. S. C. I. 1915, **34**, 711.

[7] Faerb. Ztg. 1895–1896, 441; 1898, 197, 234. For mercerizing under pressure, refer to C. Ahnert, D. R. P. 181927, 204512, 209428. For mercerizing in a vacuum, see Societe Meyer Freres, F. P. 270670.

[8] Dingl. Poly. 1897, **306**, 19; 1898, **307**, 180.

[9] J. S. C. I. 1909, **28**, 228; abst. J. Soc. Dyers Col. 1911, **27**, 126.

[10] J. S. C. I. 1904, **23**, 404; Jour. Soc. Dyers Col. 1903, **19**, 139. See their E. P. 2758, 1904; abst. J. S. C. I. 1905, **24**, 85. D. R. P. 167930, 1904; 177166, 1905. E. P. 6384, 1904; 2993, 1905; D. R. P. 177166, W. Mather, J. Huebner and W. Pope.

[11] J. S. C. I. 1909, **28**, 641; abst. C. A. 1910, **4**, 1241; Bull. Soc. Chim. 1910, **8**, 59; Chem. Zentr. 1909, **80**, II, 1284; Jahr. Chem. 1909, **62**, II, 383.

[12] In a "Manual of Dyeing," Knecht, Rawson, Lowenthal, 1910, **1**, 37, the explanation of the phenomenon of mercerization is given, as above quoted.

In yarn, however, but more especially in the piece, this luster is not apparent, because the irregular reflecting surfaces of the fibers disperse the reflected light in every direction and the impression produced in the eye is that of a dull or lusterless surface. The same holds good for cotton mercerized without tension. But if a large proportion of the fibers in a piece of calico are caused to lie in the same plane—e. g., by passing the piece through a heated calender, a lustrous or glazed surface results. The effect is not permanent because the fibers have not been set by the treatment, and on being moistened with water résumé their previous irregular positions, which results in the disappearance of the luster. But if cotton yarn is mercerized under tension, it acquires, while saturated with the caustic soda, a gelatinous, and to some extent plastic condition, so that the fibers, while becoming rounded and more translucent (and in this respect more like silk in structure), are drawn out and stretched, and become set in this position by the subsequent washing. We have consequently in the finished yarn a large proportion of stretched and straightened fibers, with a more or less round section lying parallel to each other, as in the case of spun silk, so that the inherent luster of the fiber becomes visible to the naked eye."

The mercerizing finish may be made more permanent by various after treatments. P. Krais[1] with the Bradford Dyers Association[2] and M. Petzold,[3] have advocated the use of nitrocellulose dissolved in amyl acetate, similar processes having been described by J. Bemberg,[4] E. Mueller,[5]

---

[1] E. P. 18742, 1904. U. S. P. 834913, 1906. D. R. P. 212695, 1905; abst. J. S. C. I. 1905, **24**, 887; 1909, **28**, 653; Text. Rec. 1907, **32**, 100; Text. u. Faerb. Ztg. 1906, **4**, 165.

[2] D. R. P. 212696, 1903; Belg. P. 182834, 1905. R. Ritter, D. R. P. 210499, 1907. W. Yates, E. P. 27693, 1907; D. R. P. 224343, 1908.

[3] D. R. P. 224806, 225282, 1907; 211506, 216622, 1908; Chem. Ztg. Rep. 1909, 664. H. Akyroyd and P. Krais, D. R. Anm. 6850, 1899; U. S. P. 657849, 1899. Compare J. Wilde, D. R. P. 110184. J. Ashwell, D. R. P. 181466. J. Matter, D. R. P. 215045. Fischer and Rosenfelder, F. P. 285955; D. R. P. 113928.

[4] D. R. P. 198480, 1904. E. Düring, D. R. Anm. A-18422. E. Schelling, F. P. 424434, 1911. D. Habel, D. R. P. 230669, 1909. M. Schuetze, D. R. P. 128475. M. Kohl, D. R. P. 237835, 1910. M. Wünchmann, D. R. P. 212263, 1908; 220484, 1909. G. Capron, D. R. P. 117733. F. P. 306837. P. Wolf, D. R. P. 235661, 1908. H. Gassner, D. R. P. 113929. W. Herschmann, D. R. P. 110508.

[5] D. R. P. 222777, 1909. A. Martin, D. R. P. 218774, 1908. H. Kearns, D. R. P. 138222, 1900. P. Hahn, D. R. P. 219838, 1908; D. R. Anm. 47537, 1909; 52445, 1910. F. P. 405551, 1909. E. P. 28329, 1910. H. Müller,

M. Petzold,[1] L. Chischin,[2] and F. Bayer and Co.,[3] in which the cellouse nitrates are combined with amyl formate and similar solvent combinations. The use of cellulose acetate for this purpose, either alone,[4] or combined with other cellulose esters[5] has been patented by Lilienfeld. Viscose,[6] albumen,[7] resins,[8] stearine,[9] and other bodies have been brought forward from time to time as applicable for this purpose.[10]

D. R. P. 228042, 1909. H. Schubert, D. R. Anm. 25102, 1906.

[1] D. R. Anm. 26083, 1910. O. Venter, D. R. P. 203745, 211566, 1907. A. Palmer, E. P. 20645, 1909. L. Wallach, D. R. P. 202789, 1907. Akt. Ges. Rothes Meer, D. R. P. 182937, 1906. A. Keller-Dorian, D. R. P. 185835, 1905. A. Bernhardt, D. R. P. 233514, 1909. J. Eck & Son, D. R. P. 144695; 197589, 1906; 232568, 1910.

[2] D. R. Anm. 12045, 1903. J. Matter, D. R. Anm. 39012, 1909; 42356, 1910; D. R. P. 215045, 1908. Möller-Holtkamp, D. R. P. 207813, 217022, 1907. J. Palmer, U. S. P. 765398, 1904. H. Schubert, D. R. Anm. 25102, 1906. G. de Keukelaere, D. R. P. 223925, 1909.

[3] D. R. P. 122351, abst. Wag. Jahr. 1901, II, 530; Chem. Ztg. 1901, 650. Zts. ang. Chem. 1901, 835; Jahr. Chem. 1901, 1417. D. R. P. 195315, abst. Wag. Jahr. 1908, **54,** II, 416; Chem. Zentr. 1908, **79,** I, 1103; Chem. Ztg. Rep. 1908, **32,** 180.

[4] L. Lilienfeld, U. S. P. 1031616, 1912; abst. J. S. C. I. 1912, **31,** 770; C. A. 1912, **6,** 2687. E. P. 11354, 1909; abst. J. S. C. I. 1910, **29,** 752. E. P. 18193, 1909, abst. J. S. C. I. 1910, **29,** 575. E. P. 13100, 1910; abst. J. S. C. I. 1911, **30,** 533. F. P. 408370, 1910; abst. J. S. C. I. 1910, **29,** 624. First Add. No. 12469, dated April 13, 1910, abst. J. S. C. I. 1910, **29,** 1299. Second Add. dated June 11, 1910; abst. J. S. C. I. 1910, **29,** 1371. Aust. P. 29b, 4642–10, June 21, 1909. U. S. P. 888516, 1908; abst. J. S. C. I. 1908, **27,** 683; C. A. 1908, **2,** 2866. U. S. P. 904269, 1908; abst. J. S. C. I. 1908, **27,** 1202. E. P. 4597, 1906; abst. J. S. C. I. 1907, **26,** 146. E. P. 592, 1907, abst. J. S. C. I. 1908, **27,** 73; C. A. 1908, **2,** 2018. E. P. 14483, 1903; abst. J. S. C. I. 1903, **22,** 1345. D. R. P. 175664, 1903; abst. Zts. ang. Chem. 1907, **20,** 461. D. R. P. 169782, 1904; 182773, 1904; abst. Zts. ang. Chem. 1907, **20,** 2090. D. R. P. 182773, 1904; 195315, 1905; 185456, 1906.

[5] D. R. P. 175664, 1903; abst. Wag. Jahr. 1906, **52,** II, 444; Zts. ang. Chem. 1907, **20,** 461.

[6] A. Fielding, E. P. 9849, 1903; abst. J. S. C. I. 1904, **23,** 439. For "mercerized paper," see Sci. Amer. 1917, 629.

[7] E. Duering, D. R. P. 206901, 1907; abst. Chem. Ztg. Rep. 1909, **33,** 512; Zts. ang. Chem. 1909, **22,** 609. 217679, abst. Chem. Ztg. Rep. 1910, **34,** 67; Wag. Jahr. 1910, **56,** II, 479; Zts. ang. Chem. 1910, **23,** 336. 218566, 1908; abst. Chem. Ztg. Rep. 1910, 120; Wag. Jahr. 1910, II, 479. See C. Rumpf, D. R. P. 220349, 1907; abst. Chem. Ztg. Rep. 1910, **34,** 180; Wag. Jahr. 1910, **56,** II, 481. D. R. Anm. 22188, 1907; 26012, 1908. W. Aderholdt, D. R. P. 235701, 1908; abst. Chem. Ztg. Rep. 1911, **35,** 340; Wag. Jahr. 1911, **57,** II, 468.

[8] C. Goedtler, D. R. P. 110029, 1898; abst. Chem. Ztg. 1900, **24,** 272; Wag. Jahr. 1900, **46,** II, 461; Zts. ang. Chem. 1900, **13,** 323.

[9] R. Huebner and J. H. Riley Co., E. P. 7972, 1908; abst. J. S. C. I. 1909, **28,** 520. J. Huebner, D. R. P. 226521, 1909; abst. Chem. Ztg. Rep. 1910, **34,** 540; Wag. Jahr. 1910, **56,** I, 484.

[10] Grossmann Bros. F. P. 293983, 1899.

The production of crepe effects, as by the processes of P. and C. Depoully,[1] Heilmann,[2] Schwabe[3] and others,[4] together with the moreening process of J. Empsall and E. Firth[5] are other commercial ramifications of this art. Sizing may be combined with lustering;[6] printing and creping may take place together;[7] but usually in these combination processes the chemicals recovered are so low that the method is unduly expensive, notwithstanding the saving in labor by a combination of operations.

From observations of partially mercerized cotton cloth, J. Lester[8] believes the mercerization process in the individual filaments goes on progressively from the periphery to the center. J. Huebner[9] and C. Beadle and H. Stevens[10] have studied the effect of addition of NaCl to NaOH used in mercerizing. The former found that when sodium chloride is present the shrinkage is lessened, the affinity for dyestuffs diminished, and the degree of luster impaired as compared with results under directly comparable conditions when no NaCl was added to the lye. The latter show that the proportion of NaOH absorbed by the cellulose becomes greater in the presence of NaCl, and that the addition of other soluble salts alters the hydration and NaOH absorption to a marked degree.

---

1. E. P. 28696, 1883; 8642, 1884; 15140, 1885; 5533, 1895; D. R. P. 30966, 1884; 37658, 1885.
2. Heilmann & Co., D. R. P. 83314, 1895; abst. Wag. Jahr. 1895, **41**, 987; Zts. ang. Chem. 1896, **9**, 26.
3. Schwabe & Co., D. R. P. 29504, 1897.
4. Wuerttemberg Kattun Manufaktur Heidenheim, D. R. P. 89977, 1895. Neunkirchner Druckfabriks, D. R. P. 101915.
5. J. Empsall and E. Firth, E. P. 156, 1900; abst. J. Soc. Dyers Color, 1901, **17**, 71, 78.
6. E. Heberlein, E. P. 27529, 1898. J. Dolder, E. P. 19273, 1899.
7. W. Kay and Thornliebank Co. E. P. 19388, 20308, 1894; 6112, 1897. Salis, Schwabe & Co. D. R. P. 29504, 1896. Badische Anilin & Soda Fabrik, E. P. 5469, 1899; 4534, 1900.
8. J. S. C. I. 1909, **28**, 230; abst. C. A. 1910, **4**, 1240; Chem. Zentr. 1909, **80**, I, 1836; Jahr. Chem. 1909, **62**, II, 1064; Wag. Jahr. 1909, **55**, II, 413; Zts. ang. Chem. 1909, **22**, 1038.
9. J. S. C. I. 1909, **28**, 228; Chem. Ztg. 1908, **32**, 220; Chem. Zentr. 1909, **80**, I, 1836. J. Huebner, J. S. C. I. 1908, **27**, 105; Proc. Manch. Lit. Phil. Soc. 1908, **52**, 2; abst. C. A. 1908, **2**, 1187; 1347; Chem. News, 1908, **97**, 10; Proc. Chem. Soc. 1907, **23**, 304; Bull. Soc. Chim. 1908, **4**, 1660; Rep. Chim. 1909, **9**, 238; Chem. Zentr. 1908, **79**, I, 1097; Chem. Ztg. **32**, 220; Jahr. Chem. 1905–1908, II, 3185; Meyer Jahr. Chem. 1908, **18**, 505; Wag. Jahr. 1908, **54**, II, 467; Zts. ang. Chem. 1908, **21**, 87, 1760.
10. Eighth Intl. Cong. Appl. Chem. 1912, **13**, 25; abst. C. A. 1912, **6**, 313; J. C. S. 1912, **102**, i, 947; Chem. Ztg. 1912, **36**, 1222.

I. Nakata[1] has demonstrated experimentally that the strength of cotton yarn under the mercerizing treatment is materially diminished and then increased again by thoroughly washing with water. He finds the mercerization process is most effective if the boiled yarn contains moisture to the extent of 75% on the dry yarn.

A. Dubosc[2] has described a combination lustering treatment, the cloth being mercerized under tension in NaOH in the usual manner, squeezed, and while still under tension is passed into a solution containing 100 parts of 30% copper sulfate solution, 100 parts ammonia and 300–400 parts of water. When the cloth appears brilliant and gelatinous it is again mercerized in 15° Bé. NaOH, washed, acidified and rinsed.

The preparation of alkali cellulose by such methods as those described by H. Eggert[3] and E. Block-Pimentel[4] are more properly considered under the section "Viscose" in another volume of this series.[5] Flax[6] and jute[7] may also be mercerized.

Cellulose Condensations. According to La Soie Artificielle[8] a new condensation product of cellulose results by treating it

---

[1] J. Chem. Ind. Tokyo, 1917, **20**, 1224; abst. C. A. 1918, **12**, 998; J. S. C. I. 1918, **37**, 203-A.

[2] Sealed Note, No. 674; Bull. Soc. Ind. Rouen, **41**, 337; abst. C. A. 1914, **33**, 2951. H. Lange, Chem. Ztg. 1903, **27**, 592, 735; abst. J. S. C. I. 1903, **22**, 1242; Wag. Jahr. 1903, **49**, 447. W. Herbig, Zts. Textilind. 1899–1900, **3**, 671.

[3] Kunst. 1913, **3**, 381; abst. C. A. 1914, **8**, 244. G. Lanzendorfer, E. P. 21869, 1904. A. Riley, E. P. 11818, 1905. B. Beresin, E. P. 6992, 1906.

[4] E. P. 7893, 1912. See E. P. 10851, 1904, F. Holtkamp, Moeller and E. Bucholz. E. P. 25445, 1906; T. Pickles. E. P. 4251, 1907; A. Silverwood and J. Taylor.

[5] For early work on alkali cellulose, see Sachs, Sitz. Ber. Wien. Akad. 1859, 1; Mangin, Compt. rend. 1892, **113**, 1069; Bull. Soc. bot. France, 1888, **35**, 421. Hoppe-Seyler, Ber. 1870, **4**, 15. See also, Ind. rubber, 1897, **14**, 102.

[6] E. Fremy and V. Urbain, E. P. 1816, 1882. D. R. P. 22370, 1882; abst. J. S. C. I. 1883, **2**, 276.

[7] W. Lukacs, E. P. 3103, 1883.

In the process of S. Jones (U. S. P. 1316958, 1919; abst. C. A. 1919, **13**, 3020) mercerization of cotton fibers woven with artificial silk formed of viscose is effected without injury to the viscose silk by subjecting the composite fabric to the action of a solution formed of alcohol 5.7% and 60° Tw. NaOH solution 94.3%.

[8] E. P. 9196, 1915; abst. C. A. 1916, **11**, 3159. F. P. 477655, 1914; abst. J. S. C. I. 1916, **35**, 597. X. Eschalier, E. P. 25647, 1906; abst. J. S. C. I. 1907, **26**, 1292. F. P. 374724, 1906; abst. J. S. C. I. 1907, **26**, 821; Mon. Sci. 1908, **69**, 29.

with trioxymethylene in the presence of ferric chloride or of organic acids, with or without dehydrating agents such as alum or calcium chloride. The product is stated to weigh more than the original cellulose and to liberate formaldehyde on hydrolysis.

Where cellulose is treated with ferric chloride and formaldehyde and dried under high vacuum, trioxymethylene is produced, the condensation product being formed upon stoving. This product is said to possess greater resistance to water than the original cellulose.

The process of E. Block-Pimental is similar.[1]

W. Vieweg has given a detailed description of the formaldehyde-cellulose of E. Blumer,[2] who allows a mixture of dilute alkali hydroxide of 5° Bé. strength and formaldehyde to act upon starch or cellulose for some hours in the cold, when it is heated for a short time, the product washed with water, and then with dilute acetic acid, the material being finally dried around 50°.

Cellulose and Benzene. In 1902 A. Nastukoff[3] described a compound obtained by the action of benzene upon a sulfuric acid solution of cellulose, which was at first considered as a tetraphenylcellulose, but subsequently was found to contain sulfur. The product, which when dried at the ordinary temperature in a desiccator corresponds to a tetraphenylcellulose plus two molecules of SO_2 with various amounts of water, was found to readily nitrate and sulfonate. Upon dry distillation of this compound,

[1] U. S. P. 1234720, 1917; abst. J. S. C. I. 1917, **36**, 1044; C. A. 1917, **11**, 2611. In an example of carrying the process into effect as shown in the patent, cellulose is treated with formaldehyde in the presence of ferric chloride, alum or calcium chloride, the material being then dried in a vacuum as much as possible, and after desiccation is heated in an oven. In the first phase of the reaction trioxymethylene is formed, which thereupon reacts with the cellulose in the presence of the ferric salt. The treated product is said not to lose its original appearance or strength, while resistance to aqueous liquids or water is materially increased. To 486 parts of cellulose, 90 parts of trioxymethylene is employed. See this vol., p. 420.

[2] D. R. P. 179590; abst. Papier Ztg. 1907, **32**, 309, 398; Chem. Ztg. 1907, **31**, 85; C. A. 1907, **1**, 1319; J. S. C. I. 1907, **26**, 1066; Chem. Zentr. 1907, **78**, I, 383; Wag. Jahr. 1906, **52**, II, 79; Zts. ang. Chem. 1907, **20**, 1246; Jahr. Chem. 1905–1908, II, 948. A. Nodon (E. P. 6668, 1913; abst. C. A. 1914, **9**, 2935; Kunst. 1915, **5**, 215. F. P. 453111; abst. C. A. 1914, **8**, 248; Kunst. 1913, **3**, 314) strengthens and renders cellulose rot-proof by superficial impregnation with a solution of a salt as sodium chloride, or zinc chloride, followed by the prolonged passage of an electric current. Either periodically-reversed or alternating currents may be used.

[3] J. Russ. Phys. Chem. Soc. 1902, **34**, 231, 505; abst. J. C. S. 1902, **82**, i, 362, 747; Chem. Centr. 1902, **73**, I, 1277; II, 576; Chem. News, 1903, **88**, 255; J. S. C. I. 1902, **21**, 1302; Zts. Farben u. Textchem. **1**, 633; abst Chem. Centr. 1903, **74**, I, 139.

toluene is obtained as the main product, while 45% benzoic acid is yielded upon oxidation with potassium or sodium permanganate.[1]

By varying the method of treatment of the cellulose in sulfuric acid with benzene, the product has been prepared so as to contain but a small amount (0.43%) of sulfur and this has been termed β-phenyldesoxyn to distinguish it from the former material, to which the name phenyldesoxyn was given. It appears to be derived from cellulose by the replacement of three hydrogen by three phenyl groups. With toluene, xylene and cumene, corresponding desoxyns result, which upon oxidation with permanganate forms tolyl-, xylyl- and cumyl-desoxyn and yields 20% of terephthalic, 4% terephthalic and 25% of trimellitica acid, and pyromellitic acids respectively. Prehnitic or mellophanic acids could not be found. In each of these four instances, carbonic and oxalic (about 15%) acids are also formed. The cellulose residue in each case appears to enter the benzene nucleus in the para position relative to methyl. It has been found that dextrose, like cellulose, also combines with benzene, forming apparently a compound in which three hydroxyl groups have been replaced by three phenyl radicles.

Cellulose and Phenol. It has been known for some time[2] that hard, soluble resinous products result upon the condensation of certain carbohydrates with phenols, and G. Mauthner[3] has obtained patent protection for such a process. According to his method liquid condensation products result when cotton is con-

[1] J. Russ. Phys. Chem. Soc. 1907, **39**, 1109; Zts. Farb. Ind. 1907, **6**, 701; abst. Chem. Zentr. 1907, **78**, I, 820; J. C. S. 1907, **92**, i, 413; J. S. C. I. 1907, **26**, 282; C. A. 1908, **2**, 1274; Jahr. Chem. 1905–1908, II, 1427; Zts. ang. Chem. 1907, **20**, 1782. Compare E. P. 28638, 1902; abst. J. S. C. I. 1903, **32**, 414; Chem. Ztg. 1904, **28**, 435. F. Ephraim, Ber. 1901, **34**, 2780; abst. J. C. S. 1901, **80**, i, 688; Bull. Soc. Chim. 1902, **28**, 150; Chem. Centr. 1901, **72**, II, 1008; Jahr. Chem. 1901, **54**, 1271. For glucose phenyldesoxine, see A. Nastukoff and J. Kotjukow, Bull. Soc. Chim. 1909, (4), **6**, 579; 1913, (4), **13**, 102; Jour. Russ. Phys. Chem. Soc. 1912, **44**, 1152; abst. Chem. Zentr. 1913, I, 19. F. Fischer and W. Schneider, J. S. C. I. 1920, **39**, 225-A.

[2] C. Councler, Ber. 1895, **28**, 24; abst. J. C. S. 1895, **68**, i, 164; Bull. Soc. Chim. 1895, **14**, 898; Chem. Centr. 1895, **66**, I, 481; Jahr. Chem. 1895, **48**, 1294.

[3] D. R. P. 247181; abst. Zts. ang. Chem. 1912, **25**, 1600; Chem. Zentr. 1912, **83**, II, 74; Chem. Ztg. Rep. 1912, **36**, 332; Wag. Jahr. 1912, **58**, II, 99; Friedlaender, 1910–1912, **10**, 1056. See also D. R. P. 220582; abst. Zts. ang. Chem. 1910, **23**, 957; Chem. Zentr. 1910, **81**, I, 1473; Chem. Ztg. Rep. 1910, **34**, 228; Wag. Jahr. 1910, **56**, II, 586; Friedlaender, 1910–12, **10**, 1060. D. R. P. 222512; abst. Zts. ang. Chem. 1910, **23**, 1740; Chem. Zentr. 1910, **81**, II, 122; Chem. Ztg. Rep. 1910, **34**, 298. D. R. P. 234806; abst. Zts. ang. Chem. 1911, **24**, 1336; Chem. Zentr. 1911, **82**, II, 118; Chem. Ztg. Rep. 1911, **35**, 299; Wag. Jahr. 1911, **57**, I, 5; Friedlaender, 1910–1912, **10**, 1058.

densed with phenol in the presence of mineral acids. For instance, by heating a mixture of one kilo of phenol and 100 gm. sulfuric acid with 350 gm. of cotton to 150–200°, a product is obtained useful in the preparation of lacquers, varnishes and for the impregnation of porous materials. Various products from liquid to plastic masses result by varying the proportion of reacting constituents, and the temperature and time of heating.

Hemi-Celluloses. The cotyledons of Lupin seeds contain cell-wall constituents which are easily soluble in dilute mineral acids and which are known as hemi-celluloses, the seeds of Lupinus hirsutus contain a considerable quantity of this material. After the removal of the fat from the disintegrated seeds and separation of the protein substances by means of caustic soda, a powder is obtained which resembles starch flour, and consisting about 90% of hemi-celluloses.[1] According to N. Castoro[2] there is no evidence that the hemi-celluloses of seed shells are drawn again into metabolic processes and these substances cannot, therefore, be called "reserve celluloses." Structurally, the hemi-celluloses are different from the fibrous celluloses, usually occurring in parenchyma cells. By hydrolysis they are resolved into crystalline monoses.

According to H. Euler[3] an examination of the literature on the cellulose-cleaving enzymes, celluloses or cytases, leads to the conclusion that if the group of reserve-carbohydrates or "hemi-celluloses" be excluded, no case of the fission of pure cellulose by the action of enzymes secreted either by fungi or higher plants, has as yet been recorded. On the other hand, there is abundant evidence at hand of the breaking down of true cellulose due to the action of living bacteria in fungi.[4] In general the study of the action of enzymes upon cellulose is complicated

[1] E. Schulze and N. Castoro, Zts. physiol. Chem. 1902, **37**, 40; 1903, **39**, 318; abst. Chem. Centr. 1903, **74**, I, 18; J. S. C. I. 1903, **22**, 169; Jahr. Chem. 1902, **55**, 1054; 1903, **56**, 1014; J. C. S. 1903, **84**, i, 152, 793; Bull. Soc. Chem. 1903, **30**, 664.

[2] Zts. physiol. Chem. 1906, **49**, 96; abst. C. A. 1907, **1**, 250; Chem. Centr. 1906, **77**, II, 1441; J. C. S. 1906, **90**, ii, 884; Bull. Soc. Chim. 1907, **2**, 542; Biochem. Centr. 1906, **5**, 760; Jahr. Chem. 1905–1908, II, 965.

[3] Zts. ang. Chem. 1912, **25**, 250; abst. Chem. Zentr. 1912, **83**, I, 1229; J. S. C. I. 1912, **31**, 224; C. A. 1912, **6**, 3517; J. C. S. 1912, **102**, i, 327.

[4] C. Yllner, Zts. ang. Chem. 1912, **35**, 103; abst. J. S. C. I. 1912, **31**, 122; Chem. Zentr. 1912, **83**, I, 1211; J. C. S. 1912, **102**, i, 163; C. A. 1912, **6**, 1224.

owing to the insolubility of the substratum. The author therefore has carried on his investigations with the soluble "cellulose-dextrins" derived from cellulose by the action of sulfuric acid.[1]

The hemi-celluloses as complex carbohydrates are structurally different from the fibrous celluloses, differ in physiological

---

[1] For additional data concerning hemicellulose and the pentosans, refer to E. Allen and B. Tollens, Ann. 1890, **260**, 289. R. Bauer, Ann. 1888, **248**, 140; Landw. Versuchstat. 1893, **38**, 191. S. Bey, Zts. klin. Med. 1900, **39**, 305. G. Bertrand, Compt. rend. 1892, **114**, 1492. G. Bertrand, Bull. Soc. Chim. 1891, (3), **5**, 546. C. Browne and B. Tollens, Ber. 1902, **35**, 1457. G. de Chalmot, Ber. 1893, **26**, 387, 791; abst. Chem. Centr. 1893, I, 1009; Jahr. Agric. Chem. 1895, 197; Ber. 1894, **27**, 422, 2722; Amer. Chem. J. 1894, **16**, 218, 229. G. de Chalmot, Amer. Chem. J. 1894, **15**, 276; 1895, **16**, 589. C. Councler, Jahr. Agri. Chem. 1894, 638; Chem. Ztg. 1897, **21**, 2. Duering, Jour. Landw. 1897, **45**, 79. Elfert, Bibliotheca botan. 1894, part 30. E. Fischer, Ber. 1894, **27**, 2486. G. Fownes, Ann. Chim. Phys. 1846, (3), **17**, 460. E. Flint and B. Tollens, Landw. Versuchstat. 1893, **42**, 381. G. Fraps. Amer. Chem. J. 1901, **25**, 501; abst. Chem. Centr. 1901, **72**, II, 324. P. Garros, Bull. Soc. Chim. 1894, **11**, 595; abst. Chem. Centr. 1894, **65**, II, 317. R. Gans and B. Tollens, Ann. 1888, **249**, 245. F. Goetze and Pfeiffer, Landw. Versuchstat. 1896, **47**, 59. L. Gruenhut, Zts. anal. Chem. 1901, **40**, 542. A. Guenther and Tollens, Ber. 1890, **23**, 1751. R. Hauers and B. Tollens, Ber. 1903, **36**, 3306. A. Herzfeld, Ber. 1895, **28**, 440. W. Herzfeld, Zts. Ver. Ruebenzucker-Ind. 1897, 604. W. Hoffmeister, Landw. Jahr. 1889, **18**, 767; Landw. Versuchstat. 1897, **48**, 401. R. Jaeger and E. Junger, Ber. 1902, **35**, 4440; 1903, **36**, 1222. Johnson, Jahr. Agrik. Chem. 1895, 197. K. Katsuyama, Ber. 1902, **35**, 669. H. Kiliana and F. Koehler, Ber. 1904, **37**, 1210. Krueger and Tollens, Zts. Ver. Ruebenzuckerind. 1896, 21. E. Kraft, Chem. Centr. 1902, **73**, II, 482. E. Kroeber, Jour. Landw. 1901, **48**, 357; 1902, **49**, 7. Kroeber, Rimbach and Tollens, Zts. ang. Chem. 1902, **15**, 477, 508; Zts. physiol. Chem. 1902, **36**. E. v. Lippmann, Ber. 1887, **20**, 1001. E. v. Lippmann, Ber. 1881, **14**, 1509. C. Lintner and G. Duell, Zts. ang. Chem. 1891, **4**, 538; Chem. Centr. 1891, **62**, II, 799. L. Maquenne, Compt. rend. 1889, **109**, 573. W. Maxwell, Amer. Chem. J. 1890, **12**, 51; Landw. Versuchstat. 1889, **36**, 15. F. Mann, M. Krüger and B. Tollens, Zts. ang. Chem. 1896, **9**, 33. A. Muntz, Compt. rend. 1882, **94**, 453; 1886, **102**, 624; Ann. Chim. Phys. 1882, (5), **26**, 121; 1887, (6), **10**, 566. E. Salkowski, Zts. physiol. Chem. 1892, **35**, 240; 1901, **54**, 162. A. Schoene and B. Tollens, Jour. Landw. 1901, **48**, 349. E. Schulze, E. Steiger and W. Maxwell, Zts. physiol. Chem. 1890, **14**, 227; abst. Jahr. Chem. 1889, **42**, 2087. C. Schulze and B. Tollens, Ann. 1892, **271**, 60; 1892, **271**, 55; Landw. Versuchstat. 1892, **40**, 367. E. Schulze, Ber. 1891, **24**, 2277; Zts. physiol. Chem. 1892, **16**, 387; 1894, **19**, 38; Ber. 1889, **22**, 1192; 1890, **23**, 2579; Landw. Jahr. 1892, **21**, 72; 1894, **23**, 1; Chem. Ztg. 1895, **19**, 1465. A. Schoene and B. Tollens, J. Landw. 1901, **49**, 21; abst. Chem. Centr. 1901, **72**, I, 1098. C. Scheibler, Ber. 1873, **6**, 612; 1868, **1**, 58, 108. E. Schulze and E. Steiger, Ber. 1887, **20**, 290; Landw. Versuchstat. 1889, **36**, 9; 1892, **41**, 207. T. Seliwanoff, Chem. Centr. 1889, **60**, I, 549. P. Sollied, Chem. Ztg. 1901, **25**, 1138. E. Steiger, Ber. 1886, **19**, 827; Zts. physiol. Chem. 1887, **11**, 373. J. Stoklasa, Zts. Zuckerind. 1889, **23**, 291, 387; Just. Jahr. 1899, II, 181. E. Steiger and E. Schulze, Ber. 1890, **23**, 3110. E. Stone, Ber. 1890, **23**, 2576; 1895, **28**, 1006. E. Subaschow, Zts. Ver. Ruebenzucker-Ind. 1896, 270. H. Suringar and Tollens, Jour. Landw. 1896, **44**, 355. B. Tollens. Ber. 1896, **29**, 1202; 1903, **36**, 221; Ann. 1890, **260**, 289; 1892, **271**, 60. B. Tollens and Krueger, Zts. Ver. Rubenzucker-Ind. **46**, 480. B. Tollens, Jour.

function, and by hydrolysis are readily resolved into the crystalline monoses. As a class, the hemi-celluloses are less distinctly characterized, and much more heterogeneous than the normal celluloses.

C. Stine[1] has patented a detonator charge consisting of nitrated hemi-cellulose with a primer containing an initial detonating composition.

Ash. Cellulose burns quietly with a luminous, smoky flame, leaving from 0.5%–2% of residue as ash, the major portion of which is usually silica, and half of the remainder alumina and iron oxide. In natural unpurified cotton, the ash has been stated as 0.2%–0.5%, and this amount may readily be reduced to less than 0.05% by careful purification. It has frequently been asserted that the silica found in cellulose has a distinct structural function in carrying out the life processes of the cell, and exists —in part at least—as organic silicon compounds. B. v. Ammon,[2] A. Grimaldi,[3] P. Thenard,[4] A. Landenberg[5] and W. Lange,[6] who have carefully investigated this subject from various angles, arrived independently at entirely negative conclusions.[7] Although the natural ash of cellulose seldom exceeds 2%, in some siliceous plants it may rise as high as 30%.[8]

Landw. 1896, **44**, 171. F. Ullik, Chem. Centr. 1894, II, 31. E. Votocek, Zts. Zuckerind. 1899, **23**, 229. B. Welbel and S. Zeisel, Monatsh. 1895, **16**, 283. S. Weiser and A. Zeitschek, Pflueg. Arch. 1902, **93**, 98; abst. Jahr. Chem. 1903, **56**, 1007. H. Wheeler and B. Tollens, Ann. 1889, **254**, 351. W. Windisch and R. Hasse, Wochenschr. Brauerei, 1901, **18**, 493. C. Wittmann, Botan. Centr. 1901, **87**, 373. J. Widsoe and B. Tollens, Ber. 1900, **33**, 132. K. Yoshimura, Coll. Agric. Tokio, 1895, **2**, 207. V. Zanotti, Annuario Soc. chim. Milano, 1889, 27; abst. Chem. Centr. 1899, **70**, I, 1209.

[1] U. S. P. 1313650, 1919; abst. J. S. C. I. 1919, **38**, 742-A; C. A. 1919, **13**, 2763. H. Timpe and J. Jurgens, E. P. 25400, 1910.

[2] Dissertation. Cologne, 1862; abst. Jahr. Chem. 1862, 140.

[3] Polli, Annali, 1870, **51**, 109; Gazz. Chim. Ital. 1872, **2**, II, 110; abst. Ber. 1872, **5**, 437.

[4] Compt. rend. 1870, **70**, 1412.

[5] Ber. 1872, **5**, 568; abst. Chem. News, 1872, **26**, 36; J. C. S. 1872, **25**, 910; Bull. Soc. Chim. 1872, **18**, 271; Jahr. Chem. 1872, **25**, 795.

[6] Ber. 1878, **11**, 822; abst. Chem. News, 1879, **38**, 47; J. C. S. 1878, **34**, 682; Chem. Centr. 1878, **49**, 458; Jahr. Chem. 1878, **31**, 948; Jahr. rein Chem. 1878, **6**, 48.

[7] They conducted their experiments upon the Equisetum or horsetail species, characterized by an ash high in silica, in which they endeavored to determine the presence of organic silicon compounds analogous to the corresponding carbon compounds. They showed that the functions of various plants were not disturbed by cultivation in silica-free soil.

[8] As distinguished from mechanically contained dirt, not entering into the structure of the plant.

Producing Amorphous Cellulose for Subsequent Nitration. According to the process of I. Kitsee,[1] "amorphous cellulose" may be produced "by applying an oil or fatty substance to a portion of the surface of a fibrous material and then subjecting the material to nitration, whereby only the parts which are not protected with the oily substances are nitrated." In the more rational process of L. Guiguet,[2] guncotton and nitrocellulose for smokeless powders, may be preferably formed from a cellulose precipitated from a fairly thin solution; *e. g.*, in the form of filaments, thus allowing the cellulose to be obtained in a more or less homogeneous state and practically free from impurities.

In the English patent of the Dynamite Manufacturing Co.,[3] a process for the nitration of cotton is described according to which the cellulose before esterification is converted into a fine and impalpable powder and placed in the loose form in sulfuric acid. The cellulose is allowed to remain in contact with this acid for some time, then washed with pure water and dried; or the powder may be dissolved in a mixture of sulfuric acid with water, and then precipitated by mixing with a large volume of water and finally dried. The celluloses treated by either of the above described methods become after drying, fine impalpable powders.

The process of the Dynamit A. G.[4] for the treatment of cellulose for facilitating the formation of nitrocellulose is similar, in that the cellulose as cotton is first swelled with sulfuric acid of 40° to 49° Bé. or with concentrated solution of zinc chloride, then washed to neutrality and dried in the usual manner.

The observation is worth recording that those who have worked with amorphous celluloses in the finely divided condition as above, have found a proneness to fume off in the nitrating

---

1. U. S. P. 767822, 1904; abst. J. S. C. I. 1904, **23**, 880; Mon. Sci. 1905, **62**, 16. This amorphous cellulose (I. Kitsee, U. S. P. 806348, 1905; abst. J. S. C. I. 1906, **25**, 28) is said to be excellent as an insulating material. The process of insulating consists in moistening one side of the strips with some solvent for the cellulose, moistening also the wire, and then, by means of rollers, enclosing the wire in the strips of cellulose.
2. E. P. 30075, 1913. F. P. 464028, 1913; abst. J. S. C. I. 1914, **33**, 376; C. A. 1914, **8**, 3122. See P. Girard, F. P. 438131, 1911; addn. 15399, 1912.
3. E. P. 2519, 1878. See also J. Huetter, D. R. P. 3867, 1878; abst. Dingl. Poly. 1879, **232**, 188.
4. D. R. P. 4410, 1878; abst. J. A. C. S. 1879, **1**, 303; Dingl. Poly. 1879, **232**, 188; Chem. Centr. 1879, **50**, 720. See Gocher Oehmuhle Gebr. van den Bosch, Belg. P. 190009, 1906.

mixture, coupled with an unusually low yield, due to large amounts of cotton going into solution or suspension in the nitrating fluid.

In the process of J. Kallivoda and A. Boehm,[1] one part of permanganate of potash is dissolved in ten parts of water and the solution cooled to 12° to 14°, when two to three parts of comminuted cellulose is added and the paste stirred. The reaction is considered completed when the gas evolution stops. This mass is washed until neutral and the residue mixed with one part of nitric acid of 1.3 sp. gr. and left for 12 hours. The mixture is then heated to 40°–70° on the water bath until the manganese has gone into solution as manganese nitrate and the amorphous cellulose separated as sediment. The solution is then decanted and the manganese recovered as permanganate, while the cellulose is washed until entirely neutral, ground, pressed to 30%–40% of water and dried. It is then nitrated in the customary manner and used as smokeless powder.

The invention of A. Luck and A. Durnford[2] relates to the production of nitrocellulose in a dense powdery form, which, according to the patentees, may be produced by employing a cotton or other form of cellulose whose structure has been destroyed, which is converted into a powder and then nitrated. The cellulose is first treated with "solvents," as sulfuric acid and water; zinc chloride in aqueous solution; or zinc chloride in HCl and water, the cellulose being afterwards separated from its solution in a hydrated state in the form of gelatinous granules. From sulfuric acid or zinc chloride, the cellulose is precipitated by merely diluting with water. It is recommended to keep the solution in a constant state of agitation during the precipitation process, and that the solution be largely diluted with water in order to obtain the gelatinous granules in a finer state. The precipitate is washed, and dried with constant stirring in order to facilitate the formation of a dense powder.

Lignocelluloses (Jute and Wood).[3] Lignocellulose[4] has

---

[1] D. R. P. 70067; abst. Wag. Jahr. 1893, **39**, 426; Chem. Centr. 1893, **64**, II, 1015; Zts. ang. Chem. 1893, **6**, 465; Ber. 1893, **26**, 598.

[2] E. P. 4769, 1895; abst. Chem. Centr. 1896, **67**, I, 1150; J. S. C. I. 1896, **15**, 134.

[3] "Lignose" has also been applied as a trade name for an explosive described by Trützschler-Falkenstein (Deutsche Ind. Ztg. 1875, 375; abst. Wag. Jahr. 1875, **21**, 532; Chem. Tech. Rep. 1875, **14**, I, 217), and consisting of nitroglycerol and wood fiber.

[4] For detailed development of the lignocelluloses, consult: E. Kabsch,

already been referred to as one of the three groups into which compound celluloses may be divided. In addition to comprizing

Jahrb. wiss. Bot. 1863, **3**, 357. Raspail, J. Scien. d'observat. II, p. 415. Autenrieth and Bayrhammer, Berz. Jahresber. 1822, I, 107. Braconnot, Ann. Chim. phys. 1819, (2), **12**; Gilbert's Annal. 1819, **63**, 347. Payen, Compt. rend. 1838, **7**, 1052; **8**, 51 and 169; 1839, **9**, 149; Ann. sc. nat. (2), 1839, II, 21; Mem. sur les developpements des vegetaux, p. 271. Baumhauer, J. prakt. Chem. 1844, **22**, 210; Berzelius Jahr. 1846, **25**, 585. Fromberg, Berz. Jahr. 1845, **24**, 462. Chevandier, Ann. Chim. Phys. 1844, (3), **10**, 129; Compt. rend. 1845, **20**, 138. Petersen and Schoedler, Ann. **17**, 142. Mulder, Physiol. Chem. 1844, p. 209, 475. Poumarede and L. Figuier, Compt. rend. 1846, **23**, 918; J. prakt. Chem. 1847, **42**, 25; Berz. Jahr. 1849, **28**, 340. Sacc, Ann. Chim. Phys. 1849, (3), **25**, 218. F. Schulze, Chem. Centr. 1857, 321; Jahr. Chem. 1857, 491. Mohl, Flora, 1840. Fremy, Compt. rend. **48**, p. 202, 862. Fremy and Terreil, Compt. rend. 1868, **66**, 456; Bull. soc. chim. 1868, p. 436; Ber. chem. Ges. 1877, **10**, 90. Fremy and Urbain, Compt. rend. 1882, **94**, 108; Ann. sc. nat. 1882, (6), **13**, 353. Fremy, Compt. rend. 1876, **83**, 1136. Erdmann, Lieb. Ann. **138**, p. 1; Suppl. Vol. V, p. 233. F. Bente, Ber. chem. Ges. 1875, **8**, 476; Landw. Vesuchstat. 1876, **19**, 164. A. Stutzer, Ber. chem. Ges. 1875, **8**, 575. Runge, Pogg. Ann. 1834, **31**, 65. Tiemann and Haarmann, Ber. chem. Ges. 1874, **7**, 608. Schapringer, Dingl. poly. J. 1865, **176**, 166. Wiesner, Karstens bot. Unters. 1866, I, 200. T. Thomsen, J. prakt. Chem. **19**, p. 146. F. Koch, Pharm. Ztg. Russland, 1886, **25**; Ber. chem Ges. **20**, Ref. 145. Wheeler and Tollens, Lieb. Ann. 1889, **254**, 304. Allen and Tollens, Lieb. Ann. 1890, **260**, 289. Hoppe-Seyler, Zeits. phys. Chem. 1888, **13**, 84. G. Lange, Ibid. 1889, **14**, 15, 283. M. Singer, Sitzungsber. Wien. Akad. 1882, **85**, I,.345. Czapek, Zeits. phys. Chem. 1899, **27**, 141, concerning "Hadromal." E. Gottlieb, J. prakt. Chem. 1883, **28**, 385. R. Otto, Bot. Centralbl. 1901, **86**, 210, 331. Henneberg, Lieb. Ann. **146**, p. 130. Holdefleiss, Landw. Jahrbuecher, Suppl. Vol. I, 1877. E. Kern, J. fuer Landwirtsch. 1877. Tollens and Suringar, Zeits. ang. Chem. 1896, 712, 742. F. Buehler, Chem. Centr. 1903, I, 1051. R. Bader, Chem. Ztg. 1895, p. 856. M. Potter, Annals of Botan. 1904, **18**, 121. Czapek, Ber. bot. Ges. 1899, **17**, 166. Baltzer, Just Jahresber. 1873, 295. Cross and Bevan, J. C. S. 1883, I, 19; Ber. chem. Ges. 1880, **13**, 1998; J. C. S. 1889, **55**, 199; Pharm. J. Trans. 1884, III, 570; Ber. chem. Ges. 1895, **28**, II, 1940; 1891, **24**, 1772; 1894, **26**, 2520. Lindsey and Tollens, Lieb. Ann. 1891, **267**, 370. H. Tauss, Dingl. poly. J. **273**, 286; 1890, **276**, 411. T. Seliwanoff, Chem. Centr. 1889, I, 549. G. Bertrand, Compt. rend. 1899, **129**, 1025. Kimoto, Agric. Coll. Tokio, 1902, p. 253. H. Wheeler and B. Tollens, Ber. chem. Ges. 1889, **22**, 1046. Dragen dorff, Analyse d. Pfl. 1882, p. 87, 90, 93. Schippe, Dissert. Dorpat, 1882; Just. Jahresb. 1882, I, 95. Winterstein. Zeits. physiol. Chem. 1893, **17**, 381. R. Bader, Chem. Ztg. 1895, **19**, 55. Johnson, Am. Chem. J. 1896, **18**, 214. Hoffmeister, Landw. Jahrbuecher, 1888, **17**, 259. Tollens, J. Landw. 1896, **44**, 171. Okamura, Landw. Versuch. 1894, **45**, 437. Councler, Forstl. Blaetter, 1889, p. 307; Chem. Ztg. 1892, **16**, 1719. Lange, Zeits. physiol. Chem. 1889, **14**, 15, 283. Streeb, Chem. Centr. 1893, II, 184. C. Maeule, Verhalten verholz. Memb. gegen $KMnO_4$ Habilitationsschrift, Stuttgart, 1901. L. de Lamarliere, Rev. Gen. Bot. 1903, **15**, 149. Singer, Sitz. Ber. Wien. Akad. 1882, **85**, (1), 349. Hoffmeister, Landw. Jahrbuecher, 1888, **17**, 260. Nickel, Bot. Centr. 1889, **38**, 754. Allen and Tollens, Lieb. Ann. 1891, **267**, 304. Lindsey and Tollens, Lieb. Annal. 1891, **267**, 341. Anonymous, Dingl. poly. J. **216**, 372. T. Hartig, Jahr. f. Foerster, 1861, I, 263. F. v. Hoehnel, Sitz. Ber. Wien. Akad. 1877, **76**, (I), 527. J. Wiesner, Wien. Akad. 1878, **77**, (I), 60. Ihl, Chem. Ztg. 1885, p. 266. L. Schaeffer, Ber. chem. Ges. 1869, II, 91. Niggl, Flora, 1881, 545. v. Baeyer, Lieb. Annal.

a large portion of all woody tissue, lignocellulose is contained in vegetable fibers such as jute, straw and esparto grass. The fol-

---

140. Mattirolo, Zeits. wiss. Mikrosk, 1885, II, 354. Ihl, Chem. Ztg. 1890, **14**, 1571. Lubavin, Ber. chem. Ges. 1869, II, 99. E. and H. Erdmann, Ber. chem. Ges. 1899, **32**, II, 1213. T. and D. Tomassi, Ber. chem. Ges. 1881, **14**, II, 1834. H. Molisch, Ber. botan. Ges. 1886, IV, No. 7. F. Runge, Pogg. Ann. 1834, **31**, 65. Tangl, Flora, 1874, 239. Molisch, Verhandl. zool. bot. Ges. Wien, 1887, p. 30. Wuerster, Ber. chem. Ges. 1887, p. 808. Nickel, Farbenreakt. der Kohlenstoffverbindungen, 2nd Ed. 1890, p. 51. Hegler, Flora, 1890, p. 33; Botan. Centralbl. 1889, **38**, 616. A. Piutti, Gazz. chim. ital. 1898, **28**, II, 168. Ihl, Chem. Ztg. 1890, **14**, 1571. Ellram, Chem. Centr. 1896, II, 99. E. Senft, Monatsh. Chem. 1904, **25**, 397. Ihl, Chem. Ztg. 1890, 1907. E. Covelli, Chem. Ztg. 1901, **25**, 684. A. Kaiser, Chem. Ztg. 1902, **26**, 335. Seliwanoff, Bot. Centr. 1891, **45**, 279. Nickel, Chem. Ztg. 1887, p. 1520; Bot. Centr. 1889, **38**, 753. Czapek, Zeits. phys. Chem. 1899, **27**, 153. H. Tauss, Chem. Centr. 1889, II, 445; 1890, II, 187. Ihl, Chem. Ztg. 1889, 432, 560; 1891, 201. Hancock and Dahl, Ber. chem. Ges. 1895, **28**, 1558. van Ketel, Beihefte bot. Centr. 1897, 423. Reinitzer, Zeitschr. phys. Chem. 1890, **14**, 466. Czapek, Zeits. phys. Chem. 1899, **27**, 154. Molisch, Ber. bot. Ges. 1886, **4**, 301. M. Potter, Ann. of Bot. 1904, **18**, 121. Lewakowsky, Just Jahresber. 1882, I, 422. Hancock and Dahl, Ber. chem. Ges. 1895, **28**, II, 1558. Schorler, "Isis," 1894. Berthold, Protoplasmamechanik, p. 39. T. Morawski, Chem. Centr. 1888, II, 1630. Benedikt and Bamberger, Monatsh. Chem. 1890, **11**, 260. A. Herzog, Chem. Ztg., 1896, **20**, 461. A. Cieslar, Mitteil. forstl. Versuchwes. Osterr. 1897, No. 23; Chem. Centr. 1899, I, 1214. Zetsche, Bot. Centr. 1897, **70**, 206. F. v. Faber, Ber. botan. Ges. 1904, **22**, 177. Boodle, Ann. of Bot. 1902, **16**, 180. Devaux, Soc. Linnaenne Bordeaux, April 22, 1903. Molisch, Sitz. Ber. Wien. Akad. June, 1881, Vol. 84. Sadebeck, Just Jahresber. 1887, II, 514. Molisch, Wien. Akad. 1879, I, p. 80, No. 1, 2. Belohoubek, Bot. Centr. 1884; Just. Jahresber. 1884, I, 176, II, 399. Tschirch and A. Will, Arch. Pharm. 1899, **237**, No. 5, 369. Lange, Flora, 1891, p. 393. A. Nathansohn, Jahrb. wiss. Bot. 1898, **32**, 671. Schellenberg, Jahrb. wiss. Bot. 1896, **29**, 236. Warburg, Ber. bot. Ges. 1893, **11**, 425. Sonntag, Landw. Jahrb. 1891, **21**, 839; Ber. bot. Ges. 1901, p. 138; Jahrb. wiss. Bot. 1903, **39**, 71. For data on cork substance (Suberin) consult: Payen, Compt. rend. 1868, **66**, 509. Haberlandt, Oest. botan. Zts. 1874, **24**, 229. K. Kuegler, Arch. Pharm. 1884, **222**, 217. Chevreul, Ann. Chim. Phys. 1807, (1), **62**, 323; 1815, **96**, 141; Schw. Jour. 1816, **16**, 323. Brandes, Schw. Jour. 1821, **32**, 393. Fremy and Urbain, J. Pharm. Chim. 1882, (5), **5**, 113. F. Czapek, Biochemie der Pflanzen, 1905, **1**, 574. O. Doepping, Ann. 1843, **45**, 286. Van Wisselingh, Arch. neerland, 1888, **12**, Part 1; 1893, **26**, 305; Justs botan. Jahr. 1888, I, 689; Verhandl. d. Akad. Amsterdam, 1892; Chem. Centr. 1892, II, 516. F. Flueckiger, Arch. Pharm. 1890, **228**, 690. E. Gilson, La Cellule, 1890, **6**, 87. F. v. Hoehnel, Sitzungber. Wien. Akad. 1877, **76**, I, 527. L. Brugnatelli, Crells Ann. 1787, **1**, 145. B. la Grange, Ann. Chim. Phys. 1797, (1), **23**, 42. M. v. Schmidt, Monatsh. 1904, **25**, 302. C. Istrati and A. Ostrogovich, Compt. rend. 1899, **128**, 1581. Siewert, Zts. ges. Naturwiss. 1867, **30**, 129. Braeutigam, Pharm. Centralh. 1898, **39**, No. 23. Thoms, Pharm. Centralh. 1898, **39**, 699. C. Correns, Sitzungsber. Wien. Akad. 1888, **97**, 658. L. Petit, Compt. rend. Biol. 1903, **55**, 31; Botan. Literaturbl. 1903, 280. A. Zimmermann, Zts. wiss. Mikr. 1902, **19**, 525. G. Lagerheim, Zts. wiss. Mikr. 1902, **19**, 525. A. Bayer, Ber. 1872, **5**, 1096. Kleeberg, Ann. 1891, **263**, 285. Caro, Ber. 1892, **25**, 939. Moehlau and Kahl, Ber. 1898, **31**, 251. E. Drabble and M. Nierenstein, Biochem. Jour. 1907, **2**, No. 3; Collegium, 1907, 179; Chem. Centr. 1907, II, 79.

TABLE XXIII.—VEGETABLE FIBROUS MATERIALS

		Dimensions of Fibers		Composition of Air-dried Substance								
Class	Name	Length mm.	Diam. μ	Ash	Moisture	Cellulose	Wax Oil	Resin	Water Soluble	Protein	Pectic Matter	Lignin
Pecto Celluloses	Cotton	20– 40	10–24	0.1–1.7	6–8	84–91	0.3–0.6	....	0.1–5.8	0.5–1.5	0.3–0.8	......
	Ramie	60–250	20–80	5.6	10.1	66	0.6	....	10.3	....	12.7	......
	Flax	4– 66	12–26	0.7–1.6	8–11	71–83	0.5–2.5	....	3.6–6.0	....	2.7–9.4	......
	Hemp	5– 55	16–50	0.8	8.9	78	0.6	....	3.5	....	9.3	......
	Manila	3– 12	16–32	1.0	11.9	65	0.6	....	1.0	....	21.8	......
Ligno Celluloses	Jute	1– 5	20–25	0.7	9.6–12.6	61–64	0.4	....	1.0–3.9	....	....	21–25
	Wheat Straw	....	......	4–6	10–14	44–51	1.2–1.6	....	8.5	2–3	....	22–28
	Esparto	0.5–3.5	7–18	3.3–3.7	8–10	46–50	2.1–2.7	....	10–12	....	....	26–30
	Bamboo	....	......	5	9	53	0.8	....	11	....	....	26
	Woods			About						About		
	Beech	....	......	0.5	12.6	45–53	0.4	....	2.4	1	....	30–39
	Birch	....	......	0.5	12.5	55	1.1	....	2.7	1	....	28
	Elm	....	......	0.5	10.7	48–55	0.9	....	2.5	1	....	31–38
	Linden	....	......	0.5	10.1	53	3.9	....	3.6	1	....	29
	Oak	....	......	0.5	13.1	40–48	0.9	....	12.2	1	....	26–34
	Poplar	....	......	0.5	12.1	63	1.4	....	2.9	1	....	20
	Fir	....	......	0.5	13.9	50–57	About 1	0.8–1.6	1.3	1	....	18–25
	White Pine	....	......	0.5	12.9	53–58	About 1	3–6	4.1	1	....	17–25
	Spruce	....	......	0.5	10–13	53–60	About 1	1.9–2.2	....	0.7	....	30

lowing table gives comparative data relating to various cellulose materials.[1]

The fiber of the jute, which is derived from two species of plants, *Corchorus capsularis* and *C. olitorius* (natural order Tiliaceae), is a simple tissue and is not subject to such various modifications as wood. It is, therefore, a more favorable subject for the preliminary study of the nature of lignocellulose.[2]

The plants of the Corchorus species are annuals.[3] The seeds are sown in April or May and grow to a height of 8–15 feet and have long, straight, cylindrical stems, $^1/_2$ to $^3/_4$ inch in thickness. The fiber is located between the bark and the central woody cylinder of the stem, and is surrounded by a gummy product consisting mainly of pectoses. Flowering takes place in August or September. The fiber is freed from other material by the well known process of retting. The stems, tied in bundles, are immersed in pits containing water and allowed to remain until fermentation of the gummy matter is completed, this process lasting from 7 to 30 days, the length of time depending on the age of the plants, temperature of the water and other conditions. The material is inspected at intervals during the retting treatment in order to ascertain when the fiber separates most readily. This examination is necessary, since if the fermentation be allowed to proceed too far, a weak fiber deficient in luster results. If, on

---

[1] H. Mueller, "Pflanzenfaser." The figures given for jute and wheat straw include pectic matter; for esparto and bamboo, include protein and pectic matter; and under lignin for different woods, also include pectic matter.

[2] A. Hantzsch and K. Schniter, Ber. 1887, **20**, 2033; abst. J. C. S. 1887, **52**, 925; Bull. Soc. Chim. 1888, **49**, 211; Jahr. Chem. 1887, **40**, 1343. C. Cross, E. Bevan and Barnes, Papierfabr. 1909, **7**, 155. C. Cross and E. Bevan, J. S. C. I. 1908, **27**, 1129; 1892, **11**, 966; abst. Mon. Sci. 1893, **41**, 889; Ber. 1893, **26**, R, 594; Chem. Centr. 1893, **64**, I, 407; Chem. Ztg. 1892, **16**, 1863. C. Cross, E. Bevan and C. Beadle, Ber. 1893, **26**, 2521; abst. Chem. News, 1893, **68**, 225, 235; J. C. S. 1894, **66**, i, 63; Bull. Soc. Chim. 1894, **12**, 442; Chem. Centr. 1894, **65**, I, 23; Jahr. Chem. 1893, **46**, 885; Meyer Jahr. Chem. 1893, **3**, 515; Wag. Jahr. 1893, **39**, 975. E. Chorley and W. Ramsay, J. S. C. I. 1892, **11**, 395, 872; abst. Chem. Centr. 1893, **64**, I, 189; Chem. Ztg. 1893, **17**, 653, 1709; Jahr. Chem. 1892, **45**, 2897, 2898. J. Collie, J. C. S. 1894, **65**, 262; abst. Chem. News, 1894, **69**, 81; Bull. Soc. Chim. 1894, **12**, 1448; Ber. 1894, **27**, R, 417; Chem. Centr. 1894, **65**, I, 579; Jahr. Chem. 1894, **47**, 758; Jahr. organ. Chem. 1894, **2**, 11. F. Sestini, Gazz. chim. ital. 1880, **10**, 240, 355; abst. Chem. News, 1880, **42**, 271; J. C. S. 1880, **38**, 538, 865; Ber. 1880, **13**, 1877; Jahr. Chem. 1880, **33**, 1026; Jahr. rein Chem. 1880, **8**, 488.

[3] E. Goulding and W. Dunstan, "Cotton and other Vegetable Fibers," 131, 135. See Raspail, Jour. scienc. d'observat. **2**, 415. Autenrieth and Bayerhammer, Berz. Jahr. Chem. 1822, **1**, 107.

the other hand, the fermentation process is not allowed to proceed far enough a gummy product results. When the retting is completed, the bundle is unfastened and the bast fiber removed from the wood and freed from cortex, hand labor being employed in these processes. The washed, separated fiber is dried in the sun or preferably in the shade. The dried material is made up into bundles, sorted according to quality and color, and finally packed by hydraulic presses into bales for export.

The jute fiber is from 5 to 12 feet long and of a light yellow color with a pronounced luster. According to E. Goulding and W. Dunstan,[1] each strand is composed of a large number of ultimate fibers from 2 to 5 mm. long and 0.02 to 0.25 mm. in diameter. A transverse section of a filament of jute reveals from 8 to 20 ultimate fibers. This length of fiber in the case of flax or hemp is 25 to 40 mm., which difference accounts for the structural inferiority of jute as compared with other fibers.[2]

Jute is weaker than flax or hemp and less durable. It may

---

[1] A specimen of "extra fine" Calcutta jute gave the following results upon analysis: moisture, 9.6%; ash, 0.7%; loss on α-hydrolysis, 9.1%; loss on β-hydrolysis, 13.1%; cellulose, 77.7%.

[2] Many plants of the natural orders Malvaceae and Tiliaceae yield bast fibers which resemble lignified jute fiber and are capable of replacing it in manufacture. The same method of purification is employed as with jute. The following plants have been used as jute substitutes: Abution species (yield the so-called China jute). Hibiscus species (of which the *Hibiscus cannabinus* is grown in considerable quantities and yields a fiber called "Bimlipatam jute"). Other important plants of this species are *Hibiscus abelmoschus* and *Hibiscus esculentus* (also known as "Okra," "Awkraw" or "Bhindi"); *Hibiscus guineensis* (also known as "Ramo"); *Hibiscus lunariifolius* (also known as "Ramma"); *Hibiscus quinquelobus* (also known as "Kowe," "Corwey," "Nassim" and "West African jute"); *Hibiscus rostellatus; Hibiscus sabdariffa* (also known as "Rama"); *Hibiscus squamosus; Hibiscus tiliaceus* (also known as "Baffoodo julo"). In addition, plants of the following species give fibers which may act as jute substitutes: Honckenya ficifolia (natural order Tiliaceae) also known as "Napunti," "Potepo" or "Bolobolo;" Sida species (natural order Malvaceae), (*S. carpinifolia, S. rhombifolia* and *S. urens*); Triumfetta (natural order Tiliaceae), (*T. cordifolia* and *T. rhomboidea*); Urena species (natural order Malvaceae) (also known as "Na fen fe," "subwe," "Akeiri," (*Urena lobata* is known in Brazil as "Aramina fiber), another plant of this species which yields a jute substitute is *Urena sinuata* (known also as "Rama"). Cellulon, made from wood pulp (Board of Trade J. April 25, 1918; J. S. C. I. 1918, **37**, 203-R), is a substitute for jute of a different type. The pulp is conducted over drums the surfaces of which are divided into parallels corresponding to the number of the yarn to be produced. The roving, which consists of a solid mass of cellulose, is taken from the drum by a special apparatus and then twisted (finished or twined) on a spinning machine. In the Scherbach process a mixture of pulp and cotton waste or wool is spun. The pulp, or mixtures containing pulp, is obtained in fiber form by squeezing the material under high pressure through small holes in plates.

readily be dyed and is capable of combining directly with basic dyestuffs. Jute on bleaching becomes weak and brittle, and even soaking in water causes deterioration. It may be readily bleached with dilute potassium permanganate after the fiber is first washed with dilute alkali, although the process is unduly expensive. The more usual hypochlorite bath is employed in practice, when bleaching is resorted to. Bleaching tends to produce a soft product with a high luster. The process in presence of water, unless carefully conducted, weakens the fiber. Bales of jute, especially if the moisture content be high, often deteriorate during transport, the deterioration being most marked in the center of the bale, the action being considered as due to bacteria.

Jute, compared with cotton cellulose, shows a higher ratio percentage of carbon and hydrogen to oxygen.

	C	H	O
Lignocellulose (jute)............	46.0–47	5.8–6.1	47.2–47.9
Cotton cellulose................	44.4	6.4	49.3

It is impossible to fix any definite empirical formula, owing to the variations in composition which are encountered. Even the conditions under which the fiber is grown influences its composition to a marked extent. However, the higher ratio percentage of carbon and hydrogen to oxygen in lignocellulose (jute), as compared with the ratio in cotton cellulose, would indicate that the relation of cellulose to lignocellulose may be represented by supposing dehydration to have taken place in the case of the latter. This representation is in agreement with the view of Sachsse. On physiological grounds this worker suggests that lignocellulose is a product of the metabolism of cellulose. C. Cross and E. Bevan[1] favor this view. From extended researches on jute, they conclude generally that lignification is a result of the gradual modification of cellulose, in which the products formed remain combined with the parent substance.

Jute cellulose is considerably more reactive than normal cel-

[1] "Cellulose," p. 178. For the action of chlorine on lignocellulose, see C. Cross and E. Bevan, Chem. News, 1888, **58**, 215; 1891, **64**, 63; J. C. S. 1889, **55**, 199; abst. J. C. S. 1892, **62**, 129; J. S. C. I. 1891, **10**, 786; Ber. 1889, **22**, R, 62, 348; Jahr. Chem. 1888, **41**, 2326; 1889, **42**, 2106.

lulose.[1] It combines with chlorine to form a well defined, yellow, chlorinated derivative which answers to certain characteristic tests. One of these consists in treating the chlorinated fiber with sodium sulfite, when a magenta coloration is obtained. Aniline salts in aqueous solution color the jute fiber a deep golden yellow. Ferric chloride produces a brownish green color. Solutions obtained by mixing ferric chloride and potassium ferricyanide in equimolecular proportions, stain the fiber a deep blue color, and as much as 50% of the weight of pigment may be absorbed. Salts of nitraniline also produce a characteristic reaction. When jute is treated with a hot solution of *p*-nitraniline (2 cc.) in hydrochloric acid (100 cc.) a deep blood-red stain is rapidly produced. Other substances, such as many of the soluble aromatic dyestuffs, also color the jute. Iodine is rapidly absorbed by jute and the fiber stained a deep brown color. With alkylsulfonic acids, a red or blue color is obtained,[2] depending upon the amount

[1] Sachsse, "Chemie u. Physiologie der Farbstoffe, Kohlenhydrate u. Proteinsubstanzen," Leipzig, 1877. For data concerning a jute substitute called "Cellulon," see Paper, 1917, **22**, No. 13, p. 19; Paper Makers Monthly, 1918, **56**, 168.

[2] See "Lignone Reactions and Constitution," C. Cross and E. Bevan, J. Soc. Dyers and Col. 1916, **32**, 135; abst. J. S. C. I. 1916, **35**, 628; Year book Pharmacy, 1891, 91. They have found that with hydroxylamine, the maximum conbination in the case of jute lignocellulose corresponds to 0.18% of nitrogen fixed. With phloroglucinol and hydrochloric acid, it is confirmed that the color reaction only accounts for a fraction of the total combination. The major reaction is attributed to a diketo-cyclohexene group in the lignone complex, while the color reaction is accounted for by the presence of a fractional quantity of an aldehydic group, probably a derivative of hydroxyfurfural. Higher results than are afforded by the standard method are obtained by drying down an excess of a solution of phloroglucinol in dilute hydrochloric acid in presence of the lignocellulose, exposed to the air for a period of four days. Both the phenol and the acid are thereby concentrated on the fiber; in this way a figure of 8.9% was obtained with a specimen of wood meal showing 6.84% after 16 hours by the standard method. Determinations were also made with pyrogallol by the air-drying process and the fixation of 7.6% on the wood lignocellulose was recorded. Jute digested with strong (33%) hydrochloric acid for six days at ordinary temperature lost 17% by weight; this was mainly confined to the furfural-yielding constituent (β-cellulose) which passed into the acid solution with a loss of about one-third of its furfural yield. The hydrolyzed solution contained 3% of acetic acid on the original fiber, and the fiber residue after oxidation with chromic acid in presence of dilute sulfuric acid yielded 6% more; thus the effect of the treatment was a considerable increase in the total yield of volatile acid. The action of ethereal hydrogen chloride on the jute fiber was also mainly confined to the β-cellulose, but no volatile acid was obtained in the extract. Oxidation of the lignone complex in the lignocellulose by chromic acid in presence of dilute sulfuric acid, yields for the main part, simple acids, acetic, oxalic, and carbonic, in proportions varying with the quantity of chromic

of reagent used. The aromatic sulfonic acids induce the same reaction. Naphthalenesulfonic acid gives a blue color, while anthracenesulfonic acid produces a deep red color. With benzenesulfonic acid an intense deep blue color results.

Jute fiber in presence of a solution of phloroglucinol in hydrochloric acid (density 1.06) assumes a reddish violet color,[1] the color reaction, however, accounting for a fraction only of the total combination. In a quantitative study of this reaction, C. Cross and E. Bevan found that a considerable time (16 hours) was required to obtain maximum combination. With hydroxylamine

acid and the strength of the sulfuric acid. By the incipient roasting of lignocellulose and cellulose the authors have isolated maltol (methylhydroxypyrone) and suggest from this that the pyrone configuration is represented in some portion of the constitutional structure of these bodies. C. Schwalbe and E. Becker (Zts. ang. Chem. 1919, **32**, 126; abst. J. S. C. I. 1919, **38**, 408-A) have made comparative examinations of flax, hemp and spruce, utilizing the scutching wastes, consisting mainly of particles of flax and hemp woods ("sprit" or "sheave"). These were analyzed according to Schwalbe's scheme. The ash was free from manganese. The fat and wax were estimated in two ways with different results, *viz.*, by extraction with ether, followed by alcohol, and by extraction with a mixture of equal volumes of alcohol and benzene. It would appear that alcohol alone is capable of extracting certain substances other than fat, wax, and resin. In both materials the cholesterol test for resin was positive. Attempts to estimate the lignin according to König's method by dissolving out the cellulose with sulfuric acid did not give very reliable results. The following method with preliminary disintegration of the structure by hydrolysis gave concordant values, but too great reliance should not be placed on their interpretation: 1 gm. of substance was moistened with strong hydrochloric acid (sp. gr. 1.19) in a stoppered bottle and heated for some time; the stopper was then removed and the material in the bottle dried on the water bath. The hydrolyzed product was collected on an asbestos filter, washed, and the material, together with the asbestos, was digested with 50 cc. of 72% sulfuric acid at the ordinary temperature for 1–2 days. The residue was collected in a Gooch crucible, dried, weighed, ignited, and the lignin calculated by difference. Pectin was estimated by von Fellenberg's method (J. S. C. I. 1917, **36**, 1190) by means of the methyl alcohol produced on heating with dilute acids. Pentosans were estimated from the furfural value according to Tollens and Kröber, the phloroglucide precipitate being afterwards extracted with alcohol to give the methylfurfural value, the results of which, however, were somewhat variable. Cellulose was estimated by Sieber and Walther's modification of Cross and Bevan's method (J. S. C. I. 1913, **32**, 974), and since the cellulose retained the greater portion of the pentosans, these were deducted from the cellulose results. A substantial amount of acetic acid was formed on distillation with dilute sulfuric acid according to Schorger's method. The analytical results are summarized in the table below, together with the values of spruce wood for comparison. It is to be noted, however, that the woody portions of flax and hemp show a closer similarity to the dicotyledonous woods than to coniferous woods, particularly as regards their high content of pentosans and the substantial yield of acetic acid. The sum of the proximate constituents calculated from the analytical results amounts to considerably over 100% and the authors propose to reject the direct lignin values, substituting for them the average value of 20%–21% which has been established for the

they found the reaction to be incomplete, corresponding to but
wood of foliage trees, and permits of accurate generalizations.

	Calculated on Dry Substance		
	Flax Sprit	Hemp Sprit	Spruce Wood
Ash	1.40	1.20	1.00
Wax, Fat and Resin:			
(*a*) Ether extract	1.38	1.20	0.6
(*b*) Alcohol extract	1.31	1.95	0.38
(*c*) Sum of (*a*) and (*b*)	2.69	3.15	0.98
(*d*) Alcohol-benzene extract	2.34	2.23	....
Methyl value	2.68	2.55	2.33
Pectin (according to von Fellenberg)	2.68	0.98	0.14
Acetic acid (Schorger's method)	4.79	4.04	1.6
Protein, N × 6.25	2.70	2.85	1.2
Furfural	13.81	13.03	....
Pentosan	23.59	22.15	11
Methylpentosan	0.47	0.51	....
Cellulose containing pentosan	62.99	71.13	60
Cellulose corrected for pentosan	46.35	50.52	53
Lignin (residue from 72% sulfuric acid)	23.77	30.13	30

---

1. See A. Wheeler (Ber. 1907, **40,** 888; Chem. News, 1907, **95,** 299; Jour. Soc. Dyers Col. 1907, **23,** 214; Chem. Zentr. 1907, **78,** II, 186; Jahr. Chem. 1905–1908, II, 965; see also E. Grandmougin, Ber. 1907, **40,** 2453; abst. Jahr. Chem. 1905–1908, II, 966, who uses *p*-nitraniline hydrochloride. J. Hertkorn (Chem. Ztg. 1902, **36,** 632; abst. J. S. C. I. 1902, **21,** 725, 1041; J. C. S. 1902, **82,** ii, 632; Rep. Chim. 1903, **3,** 16; Chem. Centr. 1902, **73,** II, 481; Jahr. Chem. 1902, **55,** 1052) has pointed out that not only does amylsulfuric acid give a red or blue coloration with ligneous matter according to the quantity of the reagent used, but all the alkyl sulfuric acids and the aromatic sulfonic acids give the same coloration, notably the higher members of the series. Naphthalene sulfonic acid gives a blue coloration, while anthracene sulfonic acid produces a deep red with ligneous matter, cellulose giving no coloration under the same conditions. By heating benzene with sulfuric acid till sulfurous acid is evolved, a reagent is produced, which gives an intense blue with wood-pulp. Cellulose is also slightly colored by this reagent. A. Backe, Compt. rend. 1910, **150,** 541; **151,** 78; abst. C. A. 1910, **4,** 624, 1509, 2936; J. C. S. 1910, **98,** i, 225, 544; J. S. C. I. 1910, **29,** 447, 970; Bull. Soc. Chim. 1910, **7,** 1064; Chem. Zentr. 1910, **81,** I, 1387, 1647; Jahr. Chem. 1910, **63,** 1371, 1696; Wag. Jahr. 1910, **56,** II, 309. E. Erdmann and C. Schaefer, Ber. 1910, **43,** 2398; abst. C. A. 1910, **4,** 3223; J. C. S. 1910, **98,** i, 718; J. S. C. I. 1910, **29,** 1198; Bull. Soc. Chim. 1911, **10,** 445; Rep. Chim. 1911, **11,** 117; Chem. Zentr. 1910, **81,** II, 1304; Jahr. Chem. 1910, **63,** II, 418; Meyer Jahr. Chem. 1910, **20,** 253. R. Benedikt and M. Bamberger, Monatsh. 1890, **11,** 260; abst. Chem. News, 1892, **65,** 21; J. C. S. 1890, **58,** 1474; J. S. C. I. 1890, **9,** 1156; Bull. Soc. Chim. 1891, **5,** 535; Ber. 1890, **23,** R, 649; Chem. Centr. 1890, **61,** II, 608; Chem. Zts. 1890, **14,** 872; Jahr. Chem. 1890, **43,** 2555; Wag. Jahr. 1890, **36,** 1156; Zts. ang. Chem. 1890, **3,** 741. C. Cross, E. Bevan and J. Briggs, Ber. 1907, **40,** 3119; abst. Chem. News, 1907, **96,** 40; J. C. S. 1907, **92,** i, 750; J. S. C. I. 1907, **26,** 941; Bull. Soc. Chim. 1908, **4,** 903; Rep. Chim. 1907, **7,** 450; Chem. Zentr. 1907, **78,** II, 1362; Jahr. Chem. 1905–1908, II, 966; Wag. Jahr. 1907, **53,** 506; Zts. ang. Chem. 1908, **21,** 1184; Biochem. Centr. 1907, **6,** 513.

0.18% of nitrogen fixed. The major reaction is attributed by them to be due to a diketocyclohexene group in the lignone complex, while the color reaction is accounted for by the presence of a very small quantity of an aldehydic group—probably a derivative of hydroxyfurfural. Jute contains 3 to 4% of methoxyl group as estimated by Zeisel's method.

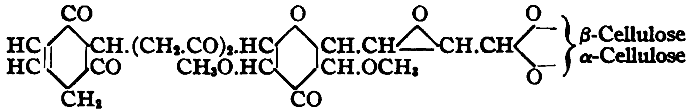
When exposed to the action of hydrolyzing agents, jute is partially resolved into soluble bodies, furfuraldehyde having been found among the products of decomposition. C. Cross and E. Bevan in treating jute with 33% hydrochloric acid for six days at ordinary temperature, find a loss of 17% in the weight of the fiber. This is mainly confined to the furfural-yielding constituents which pass into the acid solution with the loss of about one-third of its furfural yield. The hydrolyzed solution contains 3% of acetic acid on the original fiber, and the residue, after oxidation with chromic acid in presence of sulfuric acid, yields a further 6% of acetic acid. On boiling with dilute alkaline solutions (3 to 4% caustic soda) at high temperatures (140°–180°), the jute is resolved into cellulose and bodies of an acetic nature. Among the latter is acetic acid as well as complex acids of high molecular weight. However, using an elevated temperature and concentrated alkaline solutions in excess, the molecule is completely broken down, the degradation products being mainly acetic and oxalic acids. Small proportions of carbon dioxide, methane and carbon monoxide also are produced.

Nitric acid acts on jute fiber with the oxidation of the lignone portion, leaving behind a residue of cellulose. The reaction, however, requires nitrous acid for its completion, since in the presence of urea the action is a simple hydrolytic one. In the destructive oxidation with nitric acid, the main products obtained are oxalic and acetic acids.[1] The chloro-compound formed

[1] W. Thorn, Dingl. Poly. 1873, **210**, 24; abst. Chem. News, 1874, **29**, 218; J. C. S. 1874, **27**, 297; Bull. Soc. Chim. 1874, **21**, 92; Mon. Sci. 1874, **16**, 99; Chem. Centr. 1873, **44**, 744, 763; Chem. Tech. Rep. 1873, **12**, II, 140; Jahr. Chem. 1873, **26**, 1016; J. prakt. Chem. 1873, **116**, 182; Wag. Jahr. 1873, **19**, 428; Poly. Centr. 1873, **39**, 1427; Hannover. Wochenblatt f. Handel u. Gewerbe, 1873, 391. J. Lifschütz and Chem. Fabrik Grünau, Landshoff and Meyer, D. R. P. 69807; abst. Zts. ang. Chem. 1893, **6**, 465; Chem. Centr. 1893, **64**, II, 1015; Chem. Ztg. 1893, **17**, 1213; 1894, **18**, 1089; Chem. Tech. Rep. 1893, **32**, II, 272; Wag. Jahr. 1893, **39**, 427; Ber. 1893, **26**, R, 921; Mon. Sci. 1893, **42**, 200; Meyer Jahr. Chem. 1893, **3**, 366. F. Tiemann and W. Haarmann, Ber. 1874, **7**, 608; abst. Chem. News, 1874, **30**, 3; Ann. Chim.

from jute is a well defined substitution product. About one-half of the chlorine which reacts in the case of jute, appears as hydrogen chloride, thus indicating the probable absence of secondary reactions. The product after washing can be purified by precipitation from alcohol. It is apparently pure, since it has not been resolved into other substances by fractional precipitation or by further chlorination. By treatment with suitable reagents, such as sodium sulfite solution, the chlorinated complex is broken down, leaving behind a residue of cellulose. A further examination of the chlorinated compound indicates a relationship with the polyhydric aromatic phenols. Reduction yields a trichloropyrogallol. This latter reaction indicates a relation between jute lignocellulose and the tannins. The presence of groups related to the tannin complex in jute lignocellulose probably accounts for the ready absorption of various dyes, since these groups may retain their mordanting power in the complex.

The lignocellulose molecule is considered by C. Cross[1] to consist of cellulose combined with aromatic groupings. The lignocellulose complex is composed of two or more celluloses (α-cellulose and β-cellulose) in union with a lignone group and may be represented thus:



This formula, it is claimed, accounts for the quantitative action of chlorine on cellulose, and the resolution by bisulfite. The production of acetic acid in many of the reactions (hydrolysis and oxidation) which involve a breaking down of the molecule may be explained by this formula. It also takes into consideration the presence of CH_3O and OH groups, and is in agreement

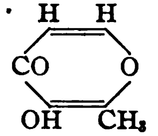
Phys. 1874, (5), **3**, 327; Bull. Soc. Chim. 1874, **22**, 385; Compt. rend. 1874, **78**, 1365; Mon. Sci. 1874, **16**, 577; Chem. Centr. 1874, **45**, 356; Jahr. Chem. 1874, **20**, 519, 888; Berl. Akad. Ber. 1874, 333; Pharm. J. Trans. (3), **4**, 996; Proc. Roy. Soc. 1874, **22**, 398; Poly. Centr. 1874, **40**, 989; Jahr. rein Chem. 1874, **2**, 399, 490.

[1] J. Soc. Dyers Col. 1914, **30**, 346; abst. J. S. C. I. 1914, **33**, 1201; C. A. 1915, **9**, 1393. For action of dilute nitric acid on lignocellulose, consult C. Cross and E. Bevan, Ber. 1891, **24**, 1772; abst. J. C. S. 1891, **60**, 1001; J. S. C. I. 1891, **10**, 831; Chem. News, 1891, **63**, 210; Chem. Centr. 1891, **62**, I, 969. For products of dry distillation of Juniperus oxycedrus, and other coniferae, consult R. Huerre, J. Pharm. Chim. 1919, **19**, 33, 65; abst. C. A. 1919, **13**, 1369.

with the results obtained on oxidation of lignocellulose by ozone.[1]

The chemical treatment of jute indicates that the lignocellulose or bastose is composed of a more resistant α-cellulose and a less resistant β-cellulose. The α-cellulose comprizes oxidized radicals, while the β-cellulose contains methoxy groups. The α-cellulose is estimated by boiling the jute fiber for five minutes with a 1% solution of caustic soda and then washing the insoluble portion free from alkali, drying and weighing. The β-cellulose may be determined as follows: The sample is boiled for one hour with 1% alkali (caustic soda) and then treated as in the case of the α-cellulose.

By heating jute or cellulose to a temperature of 100–200°, 3-hydroxy-2-methyl-γ-pyrone (maltol) is found among the products formed:



It has been suggested that the pyrone configuration represents some portion of the structure of lignocellulose.

Jute fiber is dissolved by the same solvents that attack cellulose and it is to be noted that these solvents are not able to bring about any resolution into fractions of different composition. Jute also deports itself like cellulose on nitration, the nitro-jutes being described elsewhere in detail in this work.

A preferential break-down of the lignocellulose molecule is possible by the action of various chemicals,[2] the chlorination method yielding the highest percentage of cellulose residue. This is probably due to the absence of any important secondary reactions which oxidize the cellulose complex.

A somewhat similar method has been proposed by H. Müller, which consists in alternately treating the material with cold

---

[1] C. Doree and M. Cunningham, J. C. S. 1913, **103**, 677; abst. C. A. 1913, **7**, 2385; J. S. C. I. 1913, **32**, 482; Bull. Soc. Chim. 1913, **14**, 950; Chem. Zentr. 1913, **84**, II, 246. For the jute substitute of C. Rich, see D. R. P. 308214.

[2] See C. Schwalbe, Zts. ang. Chem. 1918, **31**, 193; abst. J. S. C. I. 1918, **37**, 685-A. J. Lawrence, Met. Chem. Eng. 1917, **16**, 416; J. S. C. I. 1917, **36**, 383, 543. For chemical constitution of fir, M. Mueller and O. Heigis, D. R. P. 284681, 1914; abst. J. S. C. I. 1915, **34**, 1048; Chem. Zentr. 1915, **86**, II, 112; Zts. ang. Chem. 1915, **28**, II, 351.

bromine water, followed by an alkaline solution such as aqueous ammonia. It is usually necessary to repeat this action several times. As compared with the chlorination method, the results are generally somewhat lower. By treatment with aqueous sulfites or bisulfites at elevated temperatures under pressure, the lignone complex is removed, but there is also some attendant hydrolysis of the furfural yielding cellulose. Other methods which involve the breaking down of a portion of the cellulose as well as the lignone, are (*a*) Schultze's method using nitric acid and potassium chlorate at the room temperature, or (*b*) heating at a temperature of 60° with a 5% to 10% solution of nitric acid, or (*c*) digestion of the jute with alkali sulfite or bisulfite.

Woods from various sources which have been freed from such extraneous materials as resins, tannins, etc., have approximately constant composition, the carbon content of the separated and purified wood being in general, higher than that of normal cellulose, as will be seen from the following analyses by E. Gottlieb:[1]

TABLE XXVI.—COMPOSITION OF WOOD

Wood	Composition				Percentage Ash
	C	H	N	O	
Oak	50.16	6.02	43.45		0.37
Ash	49.18	6.27	43.98		0.57
Hornbeam	48.99	6.20	44.31		0.50
Beech	49.06	6.11	0.09	44.17	0.57
Birch	48.88	6.06	0.10	44.67	0.29
Fir	50.36	5.92	0.05	43.39	0.28
Pine	50.31	6.20	0.04	43.08	0.37

Wood is the lignified tissue of perennial stems, and in consequence its lignocellulose content is probably modified to a greater extent than is the case with jute. The chemistry of lignocellulose has therefore been developed in the main from the study of simple tissues such as those of the jute fiber.

Wood lignocellulose closely resembles jute lignocellulose in many of its reactions. On distillation with dilute hydrochloric

---

[1] J. prakt. Chem. 1883, (2), **136**, 385; abst. Chem. News, 1884, **49**, 115; J. C. S. 1884, **46** 477; Bull. Soc. Chim. 1884, **42**, 12; Mon. Sci. 1884, **26**, 128; Ber. 1883, **16**, 3064; Chem. Ztg. 1883, **7**, 1695; Jahr. Chem. 1883, **36**, 1773.

acid considerable quantities of furfuraldehyde are obtained in both cases. It has been shown also by Benedikt and Bamberger that a methoxy group is present, the amount varying slightly with the species of wood, and ranging between 4% to 6% of methoxy group. On account of the slight variation in the CH_3O content it has been proposed to utilize this approximate content in estimating mechanical wood pulp in unknown mixtures.[1] Wood is resolved into acetic and other acids of low molecular weight by treatment with suitable reagents. By processes involving hydrolysis with acids or alkalis, acetic acid is produced in amounts up to 10%. By drastic treatment with alkalis, considerable quantities of acetic acid are obtained, together with oxalic acid. By heating sawdust or wood chips with twice its weight of caustic potash and caustic soda at 240°–250° for one hour the main product obtained is oxalic acid. One part of cellulose will yield, under these conditions, 1.2 parts of oxalic acid.[2]

The action of chlorine on wood lignocellulose yields similar products to those obtained with jute fiber, except in the case of coniferous woods. These latter give a somewhat different color

---

[1] R. Benedikt and M. Bamberger, Monatsh. 1890, **11**, 267; abst. Chem. News, 1892, **65**, 21; J. C. S. 1890, **58**, 1474; J. S. C. I. 1890, **9**, 1156; Bull. Soc. Chim. 1891, **5**, 535; Ber. 1890, **23**, R, 649; Chem. Centr. 1890, **61**, II, 608; Chem. Ztg. 1890, **14**, 872; Jahr. Chem. 1890, **43**, 2555; Wag. Jahr. 1890, **36**, 1156; Zts. ang. Chem. 1890, **3**, 741.

[2] A. von Hedenström, Chem. Ztg. 1910, **34**, 613; 1911, **35**, 853; abst. C. A. 1911, **5**, 3729; J. C. S. 1911, **112**, i, 767; Mon. Sci. 1912, **76**, 345; Chem. Zentr. 1911, **82**, II, 748; Zts. ang. Chem. 1911, **24**, 2085. See also L. Gay-Lussac, Ann. Chim. Phys. 1829, **41**, 398; Edinb. J. Nat. Geogr. Sci. 1830, **1**, 384; Erd. J. tech. Chem. 1829, **6**, 387; Phil. Mag. 1829, **6**, 367; Pogg. Ann. Phys. 1829, **17**, 171, 528; Quart. J. Sci. 1829, **2**, 414; Schweiger's J. 1830, **58**, 87. F. Hoppe-Seyler, Zts. physiolog. Chem. **13**, 77. Capitaine and von Hertling, D. R. P. 84230; abst. Chem. Centr. 1896, **67**, I, 184; Ber. 1895, **28**, R, 1080; Wag. Jahr. 1895, **41**, 547; Zts. ang. Chem. 1895, **8**, 675; Jahr. Chem. 1895, **48**, 1148. Elektrochemische Werke, G. m. b. H., D. R. P. 144150; abst. Wag. Jahr. 1903, **49**, II, 8; Chem. Centr. 1903, **74**, II, 777; Chem. Ztg. 1903, **27**, 901; Zts. ang. Chem. 1903, **16**, 924; Chem. Zts. 1904, **3**, 166, 277. C. Graebe and H. Krafft, Ber. 1906, **39**, 794. For the production of methyl alcohol from residual products of sulfate cellulose manufacture, see H. Bergstrom, F. P. 433168, 1911. U. S. P. 1129542, 1915; abst. J. S. C. I. 1912, **31**, 123; 1915, **34**, 349. Papierfab. 1909, **8**, 970; 1912, **10**, 251; J. S. C. I. 1908, **27**, 1037; 1909, **28**, 37, 162; 1912, **31**, 278. H. Tiemann (J. Frank. Inst. 1919, **188**, 27; abst. C. A. 1919, **13**, 2118) has investigated the composition and structure of wood, and those factors which affect its drying. Analyses are recorded of the internal stresses which occur in wood as moisture is lost, and the wood passes from the green condition to the perfectly dry state.

reaction with sodium sulfite, especially in concentrated solution.

E. Heuser and C. Skioldebrand[1] have prepared lignin from spruce wood sawdust, previously extracted by ether, by hydrolyzing the cellulose with 42% HCl according to the method of Willstätter and Zechmeister. Two treatments with the strong HCl left the lignin apparently free from cellulose, giving a yield of 33.12% of dry lignin on the dry wood substance. The lignin contained, in the air-dry state, 9.25% of moisture and 0.485% of ash; it yielded no furfural on distillation with HCl, but showed a Cu value of 12.90% by Schwalbe's method. The methyl value according to Zeisel's method was 6.77%. This lignin was destructively distilled and the results are compared in the following table with those obtained from the raw wood and wood cellulose by Klason:

	Spruce Wood	Cotton Cellulose	Wood Cellulose	Lignin	
Charcoal	37.81	38.82	34.86	50.64	% by weight on dry ash-free substance
Tar	8.8	4.16	6.28	13.00	
Acetone	0.20	0.07	0.13	0.19	
Methyl alcohol	0.96	.....	0.07	0.90	
Acetic acid	3.19	1.39	2.79	1.09	
CO_2	56.50	57.87	62.90	9.60	% by volume on the gases
C_nH_{2n}	1.72	1.53	1.56	2.00	
CO	32.55	36.37	32.42	50.90	
CH_4	9.23	4.23	3.12	37.50	

In the distillation of the lignin, charring began at 270° and the reaction was most intense at 400°–450°; gas was still produced up to 627°. As in the case of wood and cellulose, the reaction was exothermic. The formation of CO_2 per unit of time was largest at the beginning of the gasification and then fell off rapidly. The lignin is distinguished from the other materials by the large production of CH_4 and CO and the small production of CO_2; thus the heating value of the gas from lignin is very high. In a similar way the yield of charcoal and tar is very high in the case of the lignin as compared with the other materials. As regards the yield of CH_3OH the result was disappointing, as it should have been three times as much as that obtained from

---

[1] Zts. ang. Chem. 1919, **32**, I, 41; abst. C. A. 1919, **13**, 2759; J. S. C. I. 1919, **38**, 215-A.

raw wood; this deficiency is attributed to the breaking up of the methoxyl groups into gases, owing to the higher temperature employed.

If the lignin be digested with dilute HCl under steam pressure, larger yields of CH_3OH can be obtained than by destructive distillation. The acetone also is probably derived from the same groups and the relative yield is low for the same reason; the acetone produced by the distillation of wood cellulose may be derived from the methylpentosans. Acetic acid is formed from the lignin, but only to the extent of one-third of the amount produced from the raw wood. Acetic acid is derived both from the cellulose and the lignin and in larger quantities from the former than from the latter; the absence of furfural-yielding groups from the lignin precludes the pentosans as the source of the acetic acid.

P. Waentig and W. Gierisch[1] have determined the degree of lignification of vegetable fibers by measuring the action of chlorine under specified conditions upon fibers containing lignin, it appears to be possible to determine the degree of lignification. The material to be chlorinated is placed in a small U-tube with ground-in stoppers, which is connected with an absorption vessel charged with 10% hydrochloric acid, through which the current of chlorine is passed and becomes saturated with moisture before entering the reaction tube. The outlet of the latter is connected with a second U-tube containing calcium chloride to retain the moisture from the reaction tube. The apparatus is weighed before the chlorination and again after the excess of chlorine has been removed by means of a current of air, and the percentage chlorine absorption is calculated from the increase in weight. Pine wood freshly ground to a powder gave in duplicate determinations chlorine values of 43.7 and 43.2. When treated by Willstätter and Zechmeister's method of hydrolysis with hydrochloric acid and subsequent extraction with alcohol and ether, this pine wood yielded 28% of lignin free from chlorine and ash. On chlorination as described, this lignin showed a chlorine value of 143.0. Finely ground rye straw showed a chlorine value of 30.5, and when hydrolyzed by the method of Willstätter and Zechmeister, left 22.4% residue containing 1.81% chlorine and

---

[1] Zts. ang. Chem. 1919, **32,** 173; abst. J. S. C. I. 1919, **38,** 530-A.

13.05% of ash, corresponding with 19.1% of lignin. This had a chlorine value of 144.7, which was almost the same as that of pine wood lignin. From a comparison of the chlorine values of lignified fibers with those of the isolated lignins it appears probable that the "lignin" is relatively unchanged in the hydrolytic process. The specific action of chlorine makes it a more suitable reagent than alkalis or acids for the oxidation or decomposition of fibers.

The following analyses of wood are recorded by W. Dore:[1]

	Red-wood	Yellow Pine	Sugar Pine	Live Oak	Blue Gum
	%	%	%	%	%
Loss at 100° C.	8.53	8.98	9.84	7.72	10.12
Benzene extract	0.29	2.02	2.56	0.30	0.06
Alcohol extract	4.14	1.36	1.71	4.00	2.24
Water-soluble	0.80	1.54	1.98	3.52	1.81
Soluble in 1% NaOH	7.84	10.47	9.13	7.15	12.25
Cellulose	47.58	48.38	48.67	47.52	51.48
Lignin	27.62	23.60	23.23	13.59	13.28
	96.80	96.35	97.12	83.80	91.24

The benzene and alcohol extracts were determined by extracting the dried wood (in the form of sawdust) for 6 hours successively with benzene and alcohol. The wood was then dried again and boiled for 3 hours with water to obtain the water-soluble constituents, and next boiled for 1 hour with 1% sodium hydroxide solution. The washed wood remaining after these treatments was, while still moist, transferred to a flask and the cellulose determined by a modification of Cross and Bevan's method. The chlorination was carried out *in vacuo;* the air was exhausted from the flask and chlorine then admitted slowly, the rate being judged by bubbling the gas through a wash-bottle. The flask was cooled in a bath of water and the flow of chlorine stopped when the saturation point was reached as indicated by the gas almost ceasing to bubble through the wash-bottle. Lignin was determined by König's method; in the case of the hard woods this method appeared to fail as shown by the low results ob-

---

1. J. Ind. Eng. Chem. 1919, **11**, 556; abst. J. S. C. I. 1919, **38**, 496-A.

tained. Cutin was not found in appreciable amount.

Four methods have recently[1] been investigated for the estimation of the lignin by the destruction of the cellulose, *viz.*, by heating under a pressure of 6–7 atmospheres for 6–7 hours with 1% hydrochloric acid; by treating the wood at the ordinary temperature with 72% sulfuric acid; by treating the wood with fuming hydrochloric acid, sp. gr. 1.21; and by the action of gaseous hydrogen chloride. According to the last method, 1 gm. of wood meal which has been extracted by alcohol-benzene, is mixed with 6 cc. of water and treated with gaseous hydrogen chloride, with cooling, until a thin fluid is obtained. After standing for at least 24 hours to complete the hydrolysis of the cellulose the residual lignin is collected in a Gooch crucible and the weight of ash-free residue ascertained. In the case of deciduous woods the hydrochloric acid methods gave rather more consistent results than the sulfuric acid method. The composition of the lignins obtained ranged between the limits C = 67.31%–71.35% and H = 5.07%–7.80%. For the estimation of hemi-celluloses, 4 gm. of wood powder is heated with 200 cc. of 0.4% sulfuric acid for 4–5 hours under different pressures, *viz.*, 0.5–0.75 atm. for alder, ash and poplar, 1 atm. for beech and willow, 2.25–2.5 atm. for birch and fir, and 3.5 atm. for pine wood. The extract is neutralized with calcium carbonate and the cupric reducing value determined; it is then fermented and the fermentable sugar × 0.9 is calculated as hexosans, while the dissolved pentosans are calculated from the difference between the pentosans in the original material and in the residue from hydrolysis. The results obtained in general showed that the total pentosan of the coniferous woods was low (10%–12% on the dry substance) as compared with the foliage woods (22%–26%). The lignin of the coniferous woods was high (28%–29%) as compared with the foliage woods (20%–26%). As regards the hemi-celluloses, the coniferous woods showed small quantities of pentosans (8%–9%) and large quantities of hexosans yielding fermentable sugars (about 13%), while the foliage woods showed large quantities of pentosans (15%–23%) and only small quantities of hexosans (3%–6%). The pure cellulose (corrected for pentosans) ranged between 39% and 45% for all the

---

[1] J. Koenig and E. Becker, Zts. ang. Chem. 1919, **32**, 155; abst. J. S. C. I. 1919, **38**, 530-A.

woods, with the exception of poplar, which showed 47%–49%. Analyses were made of the sugars produced by the hydrolysis of the hemi-celluloses of the woods. In the extracts from coniferous woods, xylose and dextrose were present in nearly equal proportions (21%–26% of the total reducing sugars); small quantities of galactose and large quantities of mannose were also found, pine woods being particularly rich in mannan. In the extracts from foliage woods (beech and birch) xylose was the main constituent, the dextrose was approximately the same as in coniferous woods, the quantity of galactose was small, and that of mannose very much smaller than in coniferous woods. The waste liquors from sulfite wood pulp contain fermentable sugars equivalent to 4%–5% of the wood, also hemi-celluloses, since the sugars may be increased to 12%–14% by the hydrolysis of the liquors with sulfuric acid. Experiments on the utilization of sulfite liquor in fodder have given encouraging results, the main points to be noted being that the liquor must be completely neutralized with calcium carbonate and lime to a faintly alkaline reaction; it must also be strongly aërated, for instance, by trickling over galvanized wire netting, and it must be evaporated at a temperature which will avoid the caramelization of the sugars. The dry basis of the fodder may be brewers' grains and hay meal, also bran, malt germs, or beet slices. 100–120 kilos of the dry fodder may be mixed with a cub. m. of liquor containing 120–130 kilos of dissolved solids. Provided it be neutralized and aërated, fermented spent wash from the sulfite liquors may be used. The sulfite fodder is readily eaten (*e. g.*, by sheep) and the soluble constituents, including the lignin, show a high percentage of assimilation.

O. Kress, S. Wells and V. Edwardes[1] have recently given an account of all the species of American woods which have been tested in the Forest Products Laboratory, showing weights per solid cub. ft. lengths of ultimate fibers, yields of pulp by sulfite and sulfate process, bleaching qualities, character and uses of pulps. The more important species of coniferous woods are: Black spruce (*Picea mariana*), excellent for sulfite and sulfate pulps; blue spruce (*P. parryana*), ditto; Engelmann spruce (*P. engelmanni*) ditto, also for mechanical pulp; red spruce (*P. rubens*), ditto; length of fiber, 3.7 mm.; Sitka spruce (*P. sitchensis*), ex-

---

[1] Paper, 1919, **24**, 914; abst. J. S. C. I. 1919, **38**, 713-A.

cellent for sulfite and sulfate, length of fiber 3.5 mm., mechanical pulp slightly greyish; white spruce (*P. canadensis*), the standard sulfite pulp wood of America, sulfate pulp of highest quality, mechanical pulp excellent, fiber length 2.8 mm.; Alpine fir (*Abies lasiocarpa*), excellent sulfite, sulfate and mechanical pulps, equivalent to spruce; Amabalis fir (*A. amabalis*), sulfite pulp fair strength, sulfate excellent, mechanical excellent strength, slightly greyish; balsam fir (*A. balsamea*), all pulps excellent, almost as good as spruce; grand fir (*A. grandis*), sulfite pulp fair strength, other pulps equivalent to spruce; noble fir (*A. nobilis*), sulfite pulp poor strength, sulfate good, mechanical excellent; red fir, (*A. magnifica*), sulfite pulp good but hard to bleach, sulfate pulp good, mechanical fair; white fir (*A. concolor*), all pulps good; Douglas fir (*Pseudotsuga taxifolia*), sulfite pulp poor color, few uses, sulfate pulp fairly strong; hemlock (*Tsuga canadensis*), sulfite pulp fair, sulfate good, mechanical fair; Western hemlock (*Tsuga heterophylla*), sulfite and sulfate pulps good, mechanical greyish; tamarack (*Larix laricina*), sulfite pulp strong but difficult to bleach—coarse, sulfate pulp good, mechanical fair; Western larch (*Larix occidentalis*) ditto; jack pine (*Pinus divaricata*), sulfite pulp useless, sulfate good, mechanical rather poor; lodgepole pine (*P. murrayyana*), sulfite good, sulfate excellent, mechanical good but pitchy; longleaf pine (*P. palustric*), sulfite unsuitable, sulfate good. The other varieties of pine are practically useless for sulfite pulps, but give excellent or good sulfate pulps; white pine (*P. strobus*) and yellow pine (*P. ponderosa*), give mechanical pulps of medium quality

The color reactions of wood with various chemical reagents in HCl solution are often characteristic, and have been summarized by F. Czapek[1] as follows:

In the destructive distillation of woods the products formed are very similar to those from jute lignocellulose. This subject has been worked out in great detail for wood, on account of the commercial importance of the products. The chief compounds distilling over are methyl alcohol, acetone and acetic acid. It is considered probable that the primary products are methyl alco-

---

[1] F. Czapek, "Biochemie der Pflanzen," Jena, 1905, 567; Ber. bot. Ges. 1899, **17**, 166; Zts. physiol. Chem. 1899, **27**, 153; abst. J. C. S. 1899, **76**, i, 560; Chem. Centr. 1899; **70**, I, 692; Jahr. Chem. 1899, **52**, 1300; Chem. Tech. Rep. 1899, **38**, 103; Apotheker Ztg. 1899, 322.

TABLE XXIX.—COLOR REACTIONS OF LIGNOCELLULOSE

Reagent	Color	Observer
Phenol (in sunlight)	Bluish green	F. Runge[1]
Phloroglucin	Violet-red	J. Wiesner[2]
Resorcin	Violet	J. Wiesner[2]
Orcin	Red-violet	v. Lippmann
Pyrocatechol	Greenish blue	J. Wiesner[2]
Pyrogallol	Blue-green	J. Wiesner and A. Ihl[3]
Guaiacol	Yellow-green	F. Czapek
Cresol	Greenish	F. Czapek
Naphthol	Greenish	A. Ihl[4]
Thymol	Green	
Anisol	Greenish yellow	
Anethol	Greenish yellow	
Indol, skatol or carbazol	Cherry-red	A. v. Bayer and Niggl,[5] Mattirolo[6]
Pyrrol or methylheptenon	Red	A. Ihl,[7] E. and H. Erdman[8]
Phenol and $KClO_3$	Bluish green	T. and D. Tommasi[9]
α-Naphthol and $KClO_3$	Greenish	H. Molisch[10]
Aniline salts	Yellow	Tangl[11]
p-Toluidine	Red	M. Singer[12]
Xylidine, *m*-phenylenediamine	Red	H. Molisch[13]
Dimethyl-*p*-phenylenediamine	Red	C. Wurster[14]
α- and β-Naphthylamine	Yellow	E. Nickel[15]
Toluylenediamine and thallin sulfate	Yellow	Hegler[16]
o-Bromphenetidin chloride	Yellow	A. Piutti[17]
Lepidin	Yellow	A. Ihl[18]
Diphenylamine	Yellow	Ellram[19]
Thiophene	Green	A. Ihl[20]
Amyl alcohol and concentrated H_2SO_4	Red or blue	Kaiser[21]
p-Nitrobenzylidene acetophenone and *p*-amidobenzylidene Acetophenone	Brownish red	H. Rupe and A. Porai-Kochitz[22,23]

hol, acetic acid, furfuraldehyde and pyrogallol derivatives, and

1. Pogg. Ann. Phys. 1834, **31,** 65. See also J. prakt. Chem. 1850, **51,** 95.
2. Wien. Akad. Ber. 1878, **77,** I, 60; abst. Dingl. Poly. 1878, **227,** 397; J. C. S. 1878, **34,** 612; Jahr. Chem. 1878, **31,** 1086; Zts. anal. Chem. 1878, **17,** 511. See also R. v. Wagner, Dingl. Poly. 1878, **228,** 173; J. prakt. Chem. 1851, **52,** 451; J. C. S. 1878, **34,** 397. A. Kielmeyer, Dingl. Poly. 1878, **227,** 584.
3. Chem. Ztg. 1885, **9,** 266; abst. Chem. Tech. Rep. 1885, **24,** II, 263; Wag. Jahr. 1885, **31,** 1054; Indbl. 1885, 102.
4. L. Schaeffer (Ber. 1869, **2,** 91; abst. Chem. News, 1870, **21,** 58; Bull. Soc. Chim. 1869, **12,** 313; Jahr. Chem. 1869, **22,** 485). M. Niggl, Chem. Ztg. 1887, **15,** 201, 289, 563; abst. J. S. C. I. 1887, **6,** 306; 1888, **7,** 51; 1889, **8,** 421, 640, 914, 1012; 1890, **9,** 418, 555, 770; 1891, **10,** 165, 575, finds the reaction heightened in the presence of β-naphthol. For color reactions of starch with naphthol, thymol, cresol, guaiacol, catechol, orcin, resorcin, phloroglucin, see A. Ihl, Chem. Ztg. 1887, **11,** 19; abst. J. C. S. 1887, **52,** 534; Jahr. Chem. 1887, **40,** 2460.
5. Flora, 1881, 545.
6. Zts. wiss. Mikro. 1885, **2,** 354.
7. Chem. Ztg. 1890, **14,** 1571; abst. J. S. C. I. 1891, **10,** 165; Ber. 1891, **24,** R, 220; Chem. Centr. 1890, **61,** II, 1028; Jahr. Chem. 1890, **43,** 2554. N. Lubavin, Ber. 1869, **2,** 99; abst. Chem. News, 1869, **20,** 129; Jahr. Chem. 1869, **22,** 623.
8. Ber. 1899, **32,** 1213; abst. J. C. S. 1899, **76,** i, 621; J. S. C. I. 1899, **18,** 604; Bull. Soc. Chim. 1899, **22,** 717; Chem. Centr. 1899, **70,** I, 1247; Jahr. Chem. 1899, **52,** 2057.
9. T. and D. Tomassi, Ber. 1881, **14,** 1834; abst. J. C. S. 1882, **42,** 245; Jahr. Chem. 1881, **34,** 1229; Jahr. rein Chem. 1881, **9,** 266.
10. Ber. botan. Ges. 1886, **4,** 301; Dingl. Poly. 1886, **261,** 135; Zts. anal. Chem. 1887, **26,** 258; abst. Chem. News, 1888, **57,** 71; J. C. S. 1886, **50,** 1088; 1887, **52,** 692; J. S. C. I. 1886, **5,** 508; Chem. Centr. 1887, **58,** 366; Jahr. Chem. 1886, **39,** 2172; Wag. Jahr. 1886, **32,** 891; Pharm. Centralh. 1886, **28,** 718.
11. Flora, 1874, 239.
12. Sitz. Ber. Wien. Akad. 1882, **85,** 349; Monatsh. 1882, **3,** 395; abst. J. C. S. 1882, **42,** 1122; J. S. C. I. 1882, **1,** 404; 1883, **2,** 89; Ber. 1882, **15,** 2272; Chem. Tech. Rep. 1883, **22,** I, 243; Dingl. Poly. 1882, **246,** 487; Wag. Jahr. 1882, **28,** 1060. For the action upon cellulose of iodine, with either sulfuric acid, calcium chloride, aluminium chloride or phosphoric acid, see Erfind u. Erfahr. 1897, **24,** 511.
13. Dingl. Poly. 1886, **261,** 135; Zts. anal. Chem. 1887, **26,** 258; abst. Chem. News, 1888, **57,** 71; J. C. S. 1886, **50,** 1088; 1887, **52,** 692; J. S. C. I. 1886, **5,** 508; Chem. Centr. 1887, **58,** 366; Jahr. Chem. 1886, **39,** 2172; Wag. Jahr. 1886, **32,** 891; Pharm. Centralh. 1886, **28,** 718.
14. Ber. 1886, **19,** 3217; 1887, **20,** 808; abst. J. C. S. 1887, **52,** 620; J. S. C. I. 1887, **6,** 565; Bull. Soc. Chim. 1887, **48,** 76; Chem. Centr. 1887, **58,** 735; Jahr. Chem. 1887, **40,** 2467; Wag. Jahr. 1887, **33,** 1178; Papier Ztg. 1887, 599, 666, 748; Zts. Chem. Ind. 1887, **2,** 25.
15. Farbenreakt. der Kohlenstoffverb. 1890, 51; Botan. Centr. 1889, **38,** 754; Chem. Ztg. 1893, **17,** 1209, 1243; abst. J. S. C. I. 1890, **9,** 904; 1893, **12,** 869; 1894, **13,** 423; Ber. 1889, **22,** R, 841; 1893, **26,** 831; Chem. Centr. 1889, **60,** II, 197; 1893, **64,** II, 736; Jahr. Chem. 1889, **42,** 2523; 1893, **46,** 1889. Refer to C. Cross, E. Bevan and J. Briggs, Ber. 1907, **40,** 3119; Chem. Ztg. 1907, **31,** 725; abst. J. S. C. I. 1907, **26,** 941, 942; C. Cross and E. Bevan, J. Soc. Dyers Col. 1916, **32,** 135. J. S. C. I. 1893, **12,** 105.
16. Flora, 1890, 33; Botan. Centr. 1889, **38,** 616.
17. Gazz. chim. Ital. 1898, **28,** 168; abst. J. C. S. 1899, **76,** ii, 340;

methoxy derivatives. If it is true, as has been stated, that the

J. S. C. I. 1899, **18,** 76; Chem. Centr. 1899, **69,** II, 990; Jahr. Chem. 1898, **51,** 1377.

18. Chem. Ztg. 1890, **14,** 1707; abst. J. S. C. I. 1891, **10,** 165; Ber. 1891, **24,** R, 47; Chem. Centr. 1891, **62,** I, 212; Jahr. Chem. 1890, **43,** 2555.

19. Sitzber. Naturf. Ges. Univ. Jurjew, Dorpat, 1895, **11,** 117; abst. Chem. Ztg. Rep. 1896, **20,** 164; Chem. Centr. 1896, **67,** II, 99. E. Senft, Monatsh. 1904, **25,** 397; abst. J. C. S. 1904, **86,** ii, 595; J. S. C. I. 1904, **23,** 685; Bull. Soc. Chim. 1905, **34,** 238; Chem. Centr. 1904, **75,** I, 373; Jahr. Chem. 1904, **57,** 1130.

20. Chem. Ztg. 1890, **14,** 1571; abst. J. S. C. I. 1891, **10,** 165; Ber. 1891, **24,** R, 220; Chem. Centr. 1890, **61,** II, 1028; Jahr. Chem. 1890, **43,** 2554.

21. Chem. Ztg. 1902, **26,** 335; abst. J. C. S. 1902, **82,** ii, 434; J. S. C. I. 1902, **21,** 725; Rep. Chim. 1902, **2,** 352; Chem. Centr. 1902, **73,** I, 1176; Jahr. Chem. 1902, **55,** 1052.

22. Zts. Farb. Textilind. 1906, **5,** 317; abst. J. C. S. 1906, **90,** i, 754; Chem. Centr. 1906, **77,** II, 1761; Jahr. Chem. 1905–1908, II, 2703.

23. In this connection see also, T. Seliwanoff, Botan. Centr. 1891, **45,** 279; Jour. Russ. Phys. Chem. Soc. 1889, **21,** I, 85. E. Covelli, Chem. Ztg. 1901, **25,** 684. H. Tauss, Dingl. Poly. **273,** 286; 1890, **276,** 411; Chem. Centr. 1889, **60,** II, 445; 1890, **61,** II, 187. W. Hancock and O. Dahl, Ber. 1895, **28,** 1558. v. Ketel, Beihefte Botan. Centr. 1897, 423. F. Reinitzer, Zts. physiol. Chem. 1890, **14,** 466. G. Lange, Zts. physiol. Chem. 1889, **14,** 15. V. Grafe, Monatsh. 1904, **25,** 987. S. Schapringer, Dingl. Poly. 1865, **176,** 166. v. Höhnel, Sitzungber. d. Wiener Akad. 1877, **76,** I, 527. H. Blau, Pharm. Post, 1905, **38,** 752. E. Senft, Monatsh. 1904, **25,** 397. E. Grandmougin, Zts. Farben Textilchem. 1906, **5,** 321; Ber. 1907, **40,** 2453; J. C. S. 1907, **92,** ii, 588. Hegler, Flora, 1890, **73,** 33; Botan. Centr. 1889, **38,** 616. T. Morawski, Bayer Ind. u. Gewerbebl. **20,** 641; Chem. Centr. 1888, **59,** 1630. R. Combes, Bull. Soc. Pharmacol. 1906, **13,** 293. Lewakowsky, Justs Botan. Jahrb. 1882, **1,** 422. A. Wheeler, Ber. 1907, **40,** 1888; abst. J. C. S. 1907, **92,** ii, 511. The constitutional relationship of the lignin of coniferous wood to coniferyl alcohol, $HO.C_6H_3(OCH_3).CH{:}CH.CH_2OH$, has previously been developed by P. Klason, Ark. Kemi. Min. o. Geol. 1917, **6,** 21, pp.; Chem. Zentr. 1919, **90,** I, 92; abst. J. S. C. I. 1919, **38,** 570-A (see J. S. C. I. 1898, **17,** 63). The separation of the carbohydrates from the salts of ligninsulfonic acids in the spent sulfite liquors may be effected by precipitation with calcium chloride after first precipitating the sulfuric acid by barium chloride. The calcium ligninsulfonate from fir wood has a composition represented by the formula, $C_{40}H_{44}O_{18}S_2Ca$, which may be expressed as 1 mol. of coniferyl alcohol ($C_{10}H_{12}O_3$) + 3 mols. of hydroxyconiferyl alcohol ($C_{30}H_{36}O_{12}$) +1 mol. $Ca(SO_3H)$, 2-3 mols. H_2O. By the boiling point method the value of 916 was determined for the molecular weight of the ligninsulfonate, allowance being made for the degree of dissociation; it is readily soluble in water and nearly insoluble in alcohol. Naphthylamine ligninsulfonate is obtained by treating the calcium salt with naphthylamine hydrochloride; it is a yellowish sandy powder almost insoluble in water. After the precipitation of the calcium or barium ligninsulfonate from the sulfite liquor, a further precipitate may be obtained with naphthylamine hydrochloride. This latter salt has the formula, $C_{30}H_{60}O_{14}S_2N_3$, and would correspond to a lignin of the formula $C_{29}H_{26}O_3$, containing 12.3% CH_3O, whereas the calcium salt corresponds to a lignin of the formula, $C_{40}H_{42}O_{12}$, containing 17% CH_3O. The original lignin might be regarded as being composed of equal molecules of both. The molecule apparently contains a benzene nucleus substituted in the 1.3.4-positions. On destructive distillation the lignin yielded 15% of phenols. The author favors the hypothesis

destructive distillation of cellulose does not yield methyl alcohol, it would appear that this product probably comes from the lignone grouping in the distillation of wood.[1]

When wood is digested with a boiling aqueous solution of stannous chloride, a small quantity of a compound or compounds closely related to lignocellulose is formed.[2] This product is obtainable in a crude form by extracting the stannous chloride solution with benzene or ether, a second extraction being carried out with boiling ligroin. The product separates from the petroleum upon cooling, and may be further purified by crystallization from ether and formation of bisulfite derivative. The yield of purified product is 1%–2% of the weight of the wood. Czapek considers this material as a definite compound, to which he ascribes the name of hadromal. It has a melting point of 75°–80°, and is closely allied to compounds containing the vanillin group. Hadromal, according to subsequent workers,[3] is a mixture of vanillin methylfurfural and pyrocatechol.

W. Cross and B. Tollens[4] have corroborated the work of

---

that the lignin of fir wood consists of condensed forms of more or less methylated cinnamic alcohols and allied aldehydes and acids, and the general type of substituents shows a relationship to protocatechuic acid, to which resins and tannins are also related. It is not improbable that lignin may be present in the wood in t e form of a glucoside, and it may be built up from the pentoses.

[1] P. Klason, G. von Heidenstam, O. Fagerlind and E. Norlin, Arkiv. Kem. Min. Geol. 1908, **3**, 1; No. 5, 1; No. 6, 1; No. 10, 1; abst. J. C. S. 1908, **94**, i, 717; C. A. 1908, **2**, 3280, 3281; 1909, **3**, 1810; J. S. C. I. 1908, **27**, 1080; 1909, **28**, 132; Chem. Zentr. 1908, **79**, II, 1302, 1303; 1909, **80**, I, 109; II, 1178; Chem. Ztg. Rep. 1908, **32**, 252, 270, 602; Wag. Jahr. 1908, **54**, I, 5; II, 20; Zts. ang. Chem. 1909, **22**, 1205. In investigating the products obtained from the dry distillation of cellulose obtained from various sources, the authors have shown that the velocity of this reaction begins to become considerable at about 270°, at which temperature the dry distillation of cellulose becomes an exothermic process, the heat of the reaction being about 6% of the heat of combustion of cellulose. The gases evolved during the distillation have a heating value of about 3.5% of the heat of combustion of the cellulose, and include hydrogen and aromatic hydrocarbons. Acetic acid is formed during this dry distillation, beech and birch cellulose yielding a larger amount of this acid per unit weight than either cotton, fir, or pine, cellulose.

[2] F. Czapek, Zts. physiol. Chem. 1899, **27**, 154; abst. J. C. S. 1899, **76**, i, 560; Bull. Soc. Chim. 1909, **22**, 685; Chem. Centr. 1899, **70**, I, 692; Chem. Tech. Rep. 1899, **38**, 103; Jahr. Chem. 1899, **52**, 1300; Apotheker Ztg. 1899, 322. Brown and Tollens, Ber. 1902, **35**, 1457.

[3] Sitzber. Wien. 1904, **113**, 253. For determination of the reducing power of cellulose with permanganate, see L. Kollmann, Chem. Ztg. Rep. 1910, **34**, 455; abst. J. Soc. Dyers Col. 1910, **26**, 251; J. S. C. I. 1910, **29**, 1151; Zts. oester. Papier Ind. 1909, 408; 1910, 709.

[4] Jour. Landw. 1911, **59**, 185; abst. Chem. Zentr. 1911, **82**, II, 970; C. A. 1912, **6**, 2599; Zts. ang. Chem. 1911, **24**, 1660.

Cross and Bevan, that formyl and acetyl groups undoubtedly exist in lignin, and are split off hydrolytically.

Other forms of lignocellulose are glycolignose, the substance of fir woods,[1] and glycodrupose, the substance of the stony concretion of pears.[2]

Wood Pulp.[3] The preparation of wood pulp as an intermediate product in the manufacture of paper is, of course, a very important industrial process. The coniferous woods, such as the pine, fir and spruce, are the main raw materials employed. Dicotyledenous trees as poplar, and practically all soft woods, when available, can be employed equally as well for this purpose.[3]

[1] J. Erdmann, Ann. 1866, **138**, 1; 1867, Suppl. **5**, 223; abst. Bull. Soc. Chim. 1866, **6**, 340; Jahr. Chem. 1866, **19**, 672; Chem. Centr. 1866, **37**, 401; Zts. Chem. 1866, 245; J. Pharm. (4), **3**, 478.

[2] F. Bente, Ber. 1875, **8**, 476; abst. J. C. S. 1876, **29**, 421; Bull. Soc. Chim. 1876, **25**, 278; Chem. Centr. 1875, **46**, 392; Chem. Tech. Rep. 1875, **14**, I, 116; Dingl. Poly. 1876, **217**, 235; Jahr. Chem. 1875, **28**, 785; Jahr. rein Chem. 1875, **3**, 382; Wag. Jahr. 1875, **21**, 1045.

[3] For general information on this subject, consult: E. P. 2316, 1884; abst. J. S. C. I. 1885, **4**, 242. Papier Ztg.; Chem. Trade J. **9**, 107; abst. J. S. C. I. 1891, **10**, 786. No. 772, Foreign Office Annual Series; abst. J. S. C. I. 1890, **9**, 906. Papier Ztg. 1894, 938; abst. J. S. C. I. 1884, **3**, 495. Dingl. Poly. 1883, **249**, 23, 124, 302; abst. J. S. C. I. 1883, **2**, 421. Moniteur Industriel; abst. J. S. C. I. 1896, **15**, 610. Papier Ztg. 1896, **21**, (37), 1183; abst. J. S. C. I. 1896, **15**, 579. Board of Trade Journal, May 1896, 601; abst. J. S. C. I. 1896, **15**, 371. Board of Trade Journal, Jan. 1896, 40; abst. J. S. C. I. 1896, **15**, 57. Canadian Gazette of September 26th; abst. J. S. C. I. 1895, **14**, 998. Moniteur Official de Commerce of February 14th; abst. J. S. C. I. 1895, **14**, 320. Bulletin of the French Chamber of Commerce at Montreal; Board of Trade Journal; abst. J. S. C. I. 1895, **14**, 204. Bulletin du Musee Commercial 1893; Board of Trade Journal; abst. J. S. C. I. 1894, **13**, 674. Board of Trade Journal; abst. J. S. C. I. 1893, **12**, 875. Reports Consuls of the U. S. A., May 1893, 123–128; abst. Mitscherlich Patent, J. S. C. I. 1893, **12**, 701; J. S. C. I. 1893, **12**, 793. Chem. Trade J.; J. S. C. I. 1892, **11**, 174; abst. J. S. C. I. 1893, **12**, 778. Board of Trade Journal; abst. J. S. C. I. 1893, **12**, 1074. Board of Trade Journal; abst. J. S. C. I. 1893, **12**, 635. Pharm J. 1893, 5 (July 1); abst. J. S. C. I. 1893, **12**, 619. Foreign Office Annual Series, 20, 13; abst. J. S. C. I. 1897, **16**, 1053. Toronto Globe, Oct. 7, 1898; U. S. Cons. Reps.; abst. J. S. C. I. 1899, **18**, 84. Eng. and Mining J. 1898, **66**, 514; abst. J. S. C. I. 1899, **18**, 63. Foreign Office Annual Series, No. 2062, April 1898; abst. J. S. C. I. 1898, **17**, 507. Foreign Office Annual Series, No. 2161; abst. J. S. C. I. 1898, **17**, 813. Papier Ztg. 1898, **23**, (55), 2027; abst. J. S. C. I. 1898, **17**, 788. Papier Ztg. 1898, **23**, (19), 687; abst. J. S. C. I. 1898, **17**, 688. U. S. Cons. Reps., Feb. 1899, 530; abst. J. S. C. I. 1899, **18**, 313. U. S. Cons. Reps., Feb. 1899, 322; abst. J. S. C. I. 1899, **18**, 186. Foreign Office Annual Series, No. 2299, June 1899; abst. J. S. C. I. 1899, **18**, 720. Papier Ztg. 1899, **24**, (68), 2625; abst. J. S. C. I. 1899, **18**, 853. Toronto Monetary Times, 2nd December; Board of Trade Journal; abst. J. S. C. I. 1893, **12**, 79. Industries, abst. J. S. C. I. 1893, **12**, 190. Chem. Trade J.; abst. J. S. C. I. 1893, **12**, 79. Scient. American, **76**, (23), 358; abst. J. S. C. I. 1897, **16**, 575. Bull. de l'Assoc. des Chim. de Sucr. et de Dist. 1896, **14**, 456; abst. J. S.

Wood pulp is prepared either by mechanical or chemical processes, the latter being more deep-seated in their action than the former. In the mechanical treatment, only water soluble

---

C. I. 1897, **16**, 58. Wood Pulp, 1896, **1**, (3), 61–64; abst. J. S. C. I. 1896, **15**, 833. Comm. Intelligence, May 19, 1900; abst. J. S. C. I. 1900, **19**, 575. U. S. Consular Report for June, page 386; J. S. C. I. 1892, **11**, 720. Prakt. Handbuch der Papierfabr. 1896, **42**, 1633–34; abst. J. S. C. I. 1896, **15**, 610. Cons. Rep. May 16, 1903; abst. J. S. C. I. 1903, **22**, 768. Board of Trade Journal, Dec. 26, 1901; abst. J. S. C. I. 1902, **21**, 84. Board of Trade Journal, May 14, 1903; abst. J. S. C. I. 1903, **22**, 666. U. S. Cons. Reps., Aug. 12, 1902; abst. J. S. C. I. 1902, **21**, 1166. Foreign Office Annual Series, No. 2749; abst. J. S. C. I. 1902, **21**, 514. Comm. Intelligence, Nov. 21, 1901; abst. J. S. C. I. 1901, **20**, 1161. Foreign Office Annual Series, No. 2690; abst. J. S. C. I. 1901, **20**, 958. Papier Ztg. 1901, **26**, (62), 233; abst. J. S. C. I. 1901, **20**, 925. Papier-Ztg. 1901, **26**, (31), 1159; abst. J. S. C. I. 1901, **20**, 739. Board of Trade Journal, Nov. 22, 1900, 426; abst. J. S. C. I. 1900, **19**, 1165. U. S. Cons. Reps., Aug. 1900; abst. J. S. C. I. 1900, **19**, 870. U. S. Cons. Report, July 1900; abst. J. S. C. I. 1900, **19**, 789. U. S. Cons. Reps., March 1900, 404; abst. J. S. C. I. 1900, **19**, 388. Timar's Rundschau, **3**, (43), 497–99; abst. J. S. C. I. 1900, **19**, 166. Papier Ztg. 1899, **24**, (81), 3162; abst. J. S. C. I. 1899, **18**, 1047. Board of Trade Journal, March 9, 1905; abst. J. S. C. I. 1905, **24**, 300. U. S. Cons. Rep. No. 2179, Feb. 9, 1905; abst. J. S. C. I. 1905, **24**, 254. U. S. Forest Service Circular, No. 44, abst. J. S. C. I. 1904, **26**, 164. Board of Trade Journal, Dec. 21, 1905; abst. J. S. C. I. 1906, **25**, 37. Chem. and Drug. 1905, **67**, 871–872; J. S. C. I. 1901, **20**, 734, 1008; abst. J. S. C. I. 1905, **24**, 1329. Board of Trade Journal, June 22, 1905; abst. J. S. C. I. 1905, **24**, 758. Wochenbl. f. Papierfab. 1904, **35**, 3941, 3942; abst. J. S. C. I. 1905, **24**, 148. U. S. Cons. Reps. No. 2058, Sept. 17, 1904; abst. J. S. C. I. 1904, **23**, 958. Board of Trade Journal, Feb. 25, 1904; abst. J. S. C. I. 1904, **23**, 280. Wochenbl. f. Papierfabr. 1904, **35**, (3), 162–163; abst. J. S. C. I. 1904, **23**, 127. Pulp and Paper, Nov., 1908; abst. J. S. C. I. 1908, **27**, 1129. Board of Trade Journal, March 26, 1908; abst. J. S. C. I. 1908, **27**, 352. Board of Trade Journal, Sept. 26, 1907; abst. J. S. C. I. 1907, **26**, 1063. Report of Annual Meeting, J. S. C. I. 1910, **29**, 858. Papierfabr. 1910, **9**, 61–64; abst. J. S. C. I. 1910, **29**, 230. Paper Making, 1909, **28**, 279; abst. J. S. C. I. 1909, **28**, 850. Paper Making, 1911, **30**, 376; abst. J. S. C. I. 1911, **30**, 1248. Papierfabr. 1910, **8**, 996; abst. J. S. C. I. 1910, **29**, 1245. Board of Trade Journal, Aug. 4, 1910; abst. J. S. C. I. 1910, **29**, 1004. Board of Trade Journal, May 15, 1913; abst. J. S. C. I. 1913, **32**, 530. Board of Trade Journal, June 11, 1914; abst. J. S. C. I. 1914, **33**, 745. Bull. Imp. Inst. 1914, **12**, 42–44; abst. J. S. C. I. 1914, **33**, 477. Bull. Imp. Inst. 1914, **12**, 44–45; abst. J. S. C. I. 1914, **33**, 477. Consular Reports, No. 115; abst. J. S. C. I. 1914, **33**, 915. Paper Making, 1916, **35**, 10–11; abst. J. S. C. I. 1916, **35**, 172. Board of Trade Journal, Jan. 27, 1916; abst. J. S. C. I. 1916, **33**, 192. U. S. Comm. Rept. No. 277, Nov. 27, 1915; abst. J. S. C. I. 1916, **35**, 108. J. Roy. Soc. Arts, 1915, **64**, 132; abst. J. S. C. I. 1916, **35**, 39. U. S. Commerce Report, No. 169; abst. J. S. C. I. 1915, **34**, 867. U. S. Commerce Report, No. 181, Aug. 4, 1915, abst. J. S. C. I. 1915, **34**, 867. Bull. Imp. Inst. 1916, 14, 163–167; abst. J. S. C. I. 1916, **35**, 1008. Board of Trade Journal, Feb. 17, 1916; abst. J. S. C. I. 1916, **35**, 302. Bull. Imp. Inst. 1917, **15**, 1–7; abst. J. S. C. I. 1917, **36**, 1004. Bull. Agric. Intell. 1918, **9**, 1–8; abst. J. S. C. I. 1918, **37**, 226-R. Bull. Imp. Inst. 1918, **16**, 16–24; abst. J. S. C. I. 1918, **37**, 601-A. U. S. Comm. Rep. Oct. 1, 1918; abst. J. S. C. I. 1918, **37**, 476-R. Board of Trade Journal, July 18, 1918; abst. J. S. C. I. 1918, **37**, 321-R. U. S. Com. Rep. Mar. 11, 1919; abst. J. S. C. I. 1919, **38**, 171-R. Foreign Office Annual constituents are removed, the pulp after treatment containing upwards of 30% of lignin. Such a wood pulp, owing to the impurities present, is unsuitable for many purposes, for example, the preparation of good paper. The dark color of the pulp may be reduced by bleaching, but even after excessive treatment, it is difficult to obtain a product which will retain its white color indefinitely.

In the mechanical process[1] the wood is cut into lengths of 1–4 feet. The outer bark is then removed and the wood ground to a fine state of division by forcing the blocks against revolving grindstones by the aid of hydraulic pressure. In some processes the wood is steamed before grinding. During the grinding, water flows slowly over the wood and carries off to a pit the finely divided fibrous material as it is produced.[2] The larger particles are removed by forcing the liquor through a series of wire sieves or strainers.[3] By grinding "wet" a comparatively long fiber wood pulp is obtained, dry grinding being only resorted to when an especially fine product is required. The larger portions which resist grinding may be converted into wood pulp by a chemical treatment at a comparatively low temperature.[4]

J. van Wessem,[5] in preparing mechanical wood pulp from

Series, No. 2337, 1899; abst. J. S. C. I. 1899, **18**, 876. Foreign Office Annual Series, No. 2317, July 1899; abst. J. S. C. I. 1899, **18**, 793. Foreign Office Annual Series, No. 2450, June 1900; abst. J. S. C. I. 1900, **19**, 703. Foreign Office Annual Series, No. 2401, April 1900; abst. J. S. C. I. 1900, **19**, 481. Foreign Office Annual Series, No. 2471, July 1900; abst. J. S. C. I. 1900, **19**, 798. Foreign Office Annual Series, No. 2490, July 1900; abst. J. S. C. I. 1900, **19**, 799. Foreign Office Annual Series, No. 2879; abst. J. S. C. I. 1902, **21**, 1208. Foreign Office Annual Series, No. 2879; abst. J. S. C. I. 1902, **21**, 1257. Foreign Office Annual Series, No. 3014; abst. J. S. C. I. 1903, **22**, 892. Wochenbl. f. Papierfabr. 1904, **35**, 2530–2531; abst. J. S. C. I. 1904, **23**, 879. Foreign Office Annual Series, No. 3037; abst. J. S. C. I. 1903, **22**, 980. Foreign Office Annual Series, No. 3040; abst. J. S. C. I. 1903, **22**, 980. Foreign Office Annual Series, No. 3412; abst. J. S. C. I. 1905, **24**, 758. Foreign Office Annual Series, No. 2659; abst. J. S. C. I. 1901, **20**, 864. Swedish Board of Trade Announcement; abst. J. S. C. I. 1916, **35**, 108.

[1] G. Dunstan, "Cotton and Other Fibers," 216.

[2] M. Adam, E. P. 17846, 1915; abst. C. A. 1917, **11**, 1902. In this connection compare E. P. 2018, 1910; 17714, 20220, 1911; 17427, 1912; abst. C. A. 1913, **7**, 415, 890; 1914, **8**, 416.

[3] M. Lamort, E. P. 332, 1911; abst. J. S. C. I. 1911, **30**, 798. B. Loomis, F. P. 454137, 1913; abst. J. S. C. I. 1913, **32**, 865. U. S. P. 1052675, 1913; abst. J. S. C. I. 1913, **32**, 283.

[4] A. Anderson and C. Vig, Norw. P. 28771, 1918; abst. C. A. 1918, **12**, 2686. A. Anderson, U. S. P. 1068092, 1913; abst. J. S. C. I. 1913, **32**, 864. See H. de Chaume and G. Pinard-Martineau, Belg. P. 192074, 1906.

[5] E. P. 117086, 1918; abst. C. A. 1918, **12**, 2248. D. Francke, D. R. P. 24924, 1883. F. P. Oct. 13 and Dec. 21, 1881; abst. Wag. Jahr. 1883, **29**, 1123. U. S. P. 295868.

sawdust and wood waste, grinds in presence of water, the water amounting to 60% of the weight of the wood, while the heat generated during the grinding causes 30% of this added water to evaporate. The wood is passed through a crusher to a sorting machine, where it is graded with other woods. By the aid of a screw-conveyor the crushed wood from which the coarser material has been removed, is then ground in presence of a regulated amount of water. The ground material, after subjection to hydraulic pressure, is rolled and packed for export.

To obtain a plastic material from the wet wood pulp, it is treated as follows:[1] Part of the water is first removed from the pulp by draining or by a hydroextractor, the partly dry material being then mixed with a powdered, gelatinous substance, such as gum or starch, and heated in a closed vessel at 75°–100°. The resulting pulped material is plastic and may be rolled or pressed into any desired shape. In M. Porter's patent,[2] to the wet wood pulp mixed with a small proportion of tough fibers, is added china clay, talc, aluminium resinate (to waterproof) and a binding material, such as albumin and gelatin. The mixture is moulded and dehydrated by heat.

To prepare a product of higher purity than that obtainable by mechanical means and also in order to remove the lignocellulose, it is necessary to subject the wood to chemical treatment. The soda process gives a high grade product largely used for book paper. The sulfate or Krafft process gives a strong fiber and is used for wrapping paper and other purposes. It is usually unbleached. The sulfite process gives a pulp which is employed largely in the preparation of newspapers.[3]

In the soda process,[4] the wood in 4 feet lengths, with the bark

[1] H. Jackson, E. P. 11946, 1917; abst. J. S. C. I. 1918, **37,** 53-A. C. Clark, U. S. P. 927950, 927951, 1909; abst. J. S. C. I. 1909, **28,** 905. C. Weilberg, U. S. P. 981042, 1911; abst. J. S. C. I. 1911, **30,** 204.

[2] E. P. 8184, 8325, 1909; abst. J. S. C. I. 1910, **29,** 416, 483. J. Fuller, U. S. P. 40659, 1863. M. Porter, E. P. 8325, 1909; addn. to E. P. 8184, 1909; abst. J. S. C. I. 1910, **29,** 416, 483.

[3] A. Smith, J. S. C. I. 1916, **35,** 281; abst. C. A. 1916, **10,** 2402. F. Dobson, E. P. 27188, 1912; abst. J. S. C. I. 1914, **33,** 20. Addn. to E. P. 3181, 1911; abst. J. S. C. I. 1912, **31,** 225. F. P. 439286, 1912; abst. J. S. C. I. 1912, **31,** 225.

[4] E. and T. Kittelson, Swed. P. 40894, 1916; abst. C. A. 1916, **10,** 2637. A. Behr, D. R. P. 28219; 31548, 1883; abst. Dingl. Poly. 1885, **255,** 111; J. S. C. I. 1885, **4,** 241; Papier Ztg. 1884, 1436. E. Berghoff, D. R. P. 160651, 1904; Bied. Tech. Chem. Jahr. 1904, **27,** 558. M. Faudel, Dingl. Poly.

removed, is digested in a solution of caustic soda 0.5%–4% at a temperature of 160°–200° in large digesters, and at a pressure of 10–15 atmospheres for about four hours. Superheated steam is preferably used for heating in order to maintain a high concentration. The alkaline liquid may be heated by circulating it through external heaters, the latter being heated by steam, which, as it condenses in the coil is returned to the boiler.[1] The heaters are in two or more sections and may be connected by valves with any of the digesters so that the units can be operated independently. During the heating, the alkali in the liquor is gradually neutralized for about 4–4$^1/_2$ hours. Then for approximately half an hour, no further alkali is destroyed, although the heating is continued. After this period further alkali is neutralized, the higher the temperature of digestion, the sooner this stop in the neutralization of the alkali occurs. At this stage the material has undergone sufficient heating.

Another method of determining the rate of digestion is to periodically test a sample of the alkaline liquor with slight excess of sulfuric acid. When the neutralized liquor is boiled a precipitate is formed, which in successive testings up to a certain stage, gradually diminishes in bulk. When this precipitate at successive testings no longer continues to diminish in bulk, the digestion of the wood is considered as completed. During the alkali digestion the material constituents, sap, lignocellulose, acids, etc., are dissolved by the caustic soda and pass into solution. After digestion the whole mass is blown out of the digester by its own pressure, the caustic liquor drawn off, and the cellulose washed with weaker and weaker alkaline liquids, and finally with water until neutral.

Wood in the form of sawdust or shredded material may, before the soda treatment, be leached out in an acid or neutral solution[2] in order to obtain a final product with firm and flexible

---

1876, **219**, 428; abst. J. C. S. 1876, **30**, 231. B. Blackmann, U. S. P. 369836, 530634, 530635; Pap. Ztg. 1895, **20**, 1376, 2152. J. Pfiel, E. P. 11489, 1911; abst. J. S. C. I. 1912, **31**, 584.

[1] A. Cellulosepatenter, E. P. 4278, 1915; abst. C. A. 1916, **10**, 2299. D. R. P. 288018, 1915; abst. J. S. C. I. 1916, **35**, 356. Bock, Pap. Ztg. 1892, **17**, 555. H. Bucherer, Pap. Ztg. 1905, **30**, 1350.

[2] A. Deiss and C. Fournier, F. P. 403518, 1909; abst. C. A. 1911, **5**, 1514. First addn. dated Sept. 2, 1909, to F. P. 403518, 1909; abst. J. S. C. I. 1910, **29**, 556. E. P. 23625, 1909; abst. J. S. C. I. 1910, **29**, 1101. D. R. P. 235852; abst. C. A. 1912, **6**, 1365; J. S. C. I. 1910, **29**, 84. U. S. P. 967001,

fibers. This operation is usually carried out in an open vessel or in elongated tanks into which the liquid is sprayed.[1] This treatment is usually repeated until the wood has lost nearly half its original weight.

For this preliminary treatment gaseous nitrogen oxide or nitrous acid may be employed efficiently.[2] Nitric acid, hydrogen peroxide, sodium peroxide or other oxidizing agents in a concentration of 0.5%–1% also may be used. When the acid treatment is completed the cellulose material is digested with an alkaline solution, some oxycellulose being formed during these treatments. C. Cross[3] finds that even hard woods in the form of waste, as fragments, chips, shavings, etc., can be economically treated with nitric acid to produce a good cellulose. The economy of the process is effected by a recovery of the by-products formed during the acid decomposition. These products consist in the main of

---

1910; abst. J. S. C. I. 1910, **29,** 1053. P. Sparre, D. R. P. 237081, 1910; abst. C. A. 1912, **6,** 1526, 1989; Zts. ang. Chem. 1911, **24,** 1583; Chem. Zentr. 1911, II, 411. F. P. 420640, 1910; abst. J. S. C. I. 1911, **30,** 279. E. P. 29118, 1909; abst. J. S. C. I. 1911, **30,** 80.

[1] Z. Ostenberg, U. S. P. 1220778; abst. C. A. 1917, **11,** 1749. See also Z. Ostenberg, U. S. P. 1218954, 1242030 E. P. 104173; F. P. 484442, under the topic "Cellulose and Hydrochloric Acid." A. Mitscherlich, D. R. P. 1078, 8574; abst. Chem. Ind. 1878, **1,** 318. F. Cyster, Paper, 1915, **16,** No. 22, p. 13; C. A. 1915, **9,** 3129. For the preparation and spinning of threads from strips of paper, see A. Leinveber, E. P. 10530, 1902; F. P. 320529, 1902; abst. J. S. C. I. 1903, **22,** 25, 737.

[2] C. Schwalbe, E. P. 29991, 1909. F. P. 410460, 1909; abst. J. S. C. I. 1910, **29,** 810; 1911, **30,** 416. In this manner, according to the patentee, the ligneous matter can be rendered similar to cotton, and is suitable for the manufacture of explosives, artificial silk and celluloid. E. P. 19142, 1910; abst. J. S. C. I. 1910, **29,** 1299. E. P. 18199, 1914; abst. J. S. C. I. 1915, **34,** 956. D. R. P. 282050, 1913; abst. J. S. C. I. 1915, **34,** 656; C. A. 1915, **9,** 2312. D. R. P. 204460, 1907; abst. J. S. C. I. 1908, **27,** 1220. Papierfabrikant, 1911, **9,** 1522; abst. J. S. C. I. 1912, **31,** 121. Wochenbl. Papierfab. 1912, **43,** 1454; abst. J. S. C. I. 1912, **31,** 531. Zts. ang. Chem. 1908, **21,** 302; abst. J. S. C. I. 1908, **27,** 243. Zts. ang. Chem. 1918, **31,** 50, 57; abst. J. S. C. I. 1918, **37,** 365 A. Compare D. R. P. 259691, 279622, 280317, 283199, 288720. Aust. P. 69136. U. S. P. 1153970, 1201535.

[3] E. P. 409, 1894; 8544, 8545, 1904; abst. J. S. C. I. 1905, **24,** 288, 340. U. S. P. 807250, 1905; abst. J. S. C. I. 1906, **25,** 34. F. P. 351048, 1905; abst. J. S. C. I. 1905, **24,** 908. C. Cross (E. P. 104032, 1916; abst. J. S. C. I. 1917, **36,** 383; C. A. 1917, **11,** 1902) has described a process wherein lignified materials, such as paper pulp or textiles, are treated with a solution containing 0.2%–0.5% hydroxylamine or hydroxylamine acetate in order to restore their color or to make them capable of resisting discoloration under the influence of atmospheric exposure. In E. P. 8544, 8545, 1904, cellulose or hemi-cellulose of short cellular structure obtained from cotton-seed hulls is hydrolyzed with four or five times its weight of 1%–3% sulfuric acid. The solution is filtered and neutralized with barium carbonate or chalk. After filtration, the solution is evaporated until the sugar crystallizes.

oxalic and acetic acids. To 1 part of wood, 3 parts of 10% nitric acid is added and the temperature raised to 80°, this temperature being maintained by the heat generated in the reaction. When the reaction is completed the soluble portion is removed by draining and pressing the wood, this solution being worked up for oxalic and acetic acids. The cellulose material still contains non-cellulose constituents and these are removed by a subsequent alkaline treatment, followed by bleaching where a very pure product is required. This cellulose can be nitrated with nitric acid of sp. gr. 1.5 without any sulfuric acid, and when washed after nitration the washings are utilizable as the 10% acid for the treatment of further quantities of wood.

Resinous and gummy substances may be extracted by hot water before the chemical treatment.[1] These extraneous matters may also be removed by steaming in the absence of air.[2] It has also been suggested to remove them by a retting process by means of a ferment derived from African esparto grass,[3] the process being carried out, preferably, in a vacuum.

The efficiency of the soda process is enhanced by the addition of small quantities of certain metallic substances to the solution, mercury being especially suitable.[4] In one process the boiler is filled with a dilute solution of mercuric chloride (0.001 *N*), and after mercury has been deposited, the solution is run off. The boiler is then used to greater advantage for the treatment of wood by the usual soda method. This deposition of mercury is repeated every fourteen days. In this process the soda lye

---

[1] B. Loomis, U. S. P. 1052675, 1913; F. P. 454137, 1913; abst. J. S. C. I. 1913, **32**, 283, 865. U. S. P. 1122404, 1914; abst. J. S. C. I. 1915, **34**, 222. In this method the material is treated in a closed vessel, first with hot water and then with a dilute alkaline solution, which is circulated at gradually increasing temperatures through the material, a heater, and a separator in which the matters removed from the material are separated by floating or deposition. The cleansed material is subsequently digested with alkali to reduce it to pulp.

[2] C. Schwalbe, D. R. P. 203230, 1907; abst. C. A. 1909, **3**, 714; Zts. ang. Chem. 1908, **21**, 2556; Chem. Zentr. 1908, **79**, II, 1842; Chem. Tech. Rep. 1908, **32**, 594; Wag. Jahr. 1908, **54**, II, 377; J. S. C. I. 1908, **27**, 1173.

[3] A. Deiss, E. P. 23625, 1909; abst. J. Soc. Dyers Col. 1910, **26**, 252; J. S. C. I. 1910, **29**, 1101. F. P. 403518, 1909; abst. J. S. C. I. 1910, **29**, 84.

[4] Aktiebolaget Cellulosa, E. P. 116288, 1917; abst. J. S. C. I. 1918, **37**, 651-A; C. A. 1919, **13**, 73. Compare also, E. P. 6652, 1912; abst. C. A. 1913, **7**, 3025; J. S. C. I. 1912, **32**, 284. F. P. 441186, 1912; abst. J. S. C. I 1912, **31**, 812. R. Biltz, F. P. 155014, 1883.

used is about 6% concentration and must be sulfur-free.

An important objection to the soda treatment is the fact that noxious gases are evolved during the boiling, and are due, to a large extent, to the atmospheric oxygen present in the boiler combining with decomposition products of the wood. It has been proposed[1] on this account to replace the air by carbon dioxide or nitrogen.

The soda process is comparatively expensive owing to the large amount of alkali required, the high consumption of fuel and the short life of the vessels in which the reaction is carried out.[2]

After the soda treatment and the removal by washing of free alkali from the cellulose material, the latter is bleached. This process is carried out either by the action of chlorine gas, bleaching powder or by electrolytic methods.[3] When the bleaching treatment is completed the wood pulp is washed with dilute acid or alkali.[4] The bleaching is preferably performed in a rotating

---

[1] O. Dietrich, D. R. P. 201259, 1907; abst. J. S. C. I. 1908, **27**, 1037; Zts. ang. Chem. 1908, **21**, 2233; Chem. Zentr. 1908, **79**, II, 1074. W. Burton, U. S. P. 959307. F. Buehler, D. R. P. 94467; abst. Chem. Ind. 1903, **26**, 138; Wag. Jahr. 1903, **49**, II, 543.

[2] V. Drewson, U. S. P. 492196, 505755, 1893; 730439, 1903; 1309863, 1310509; abst. J. S. C. I. 1903, **22**, 817. U. S. P. 731290, 1903; abst. J. S. C. I. 1903, **22**, 876. U. S. P. 789416, 789417, 789418, 1905; abst. J. S. C. I. 1905, **24**, 633. U. S. P. 789887, 1905; abst. J. S. C. I. 1905, **24**, 1028. F. P. 344692, 1904; abst. J. S. C. I. 1904, **23**, 1233. U. S. P. 853943, 1907; abst. J. S. C. I. 1907, **26**, 713. U. S. P. 996225, 1911; abst. J. S. C. I. 1911, **30**, 950. U. S. P. 1229422, 1917; abst. J. S. C. I. 1917, **36**, 923. U. S. P. 1283113, 1283114, 1917; abst. C. A. 1919, **13**, 187; J. S. C. I. 1919, **38**, 71-A. U. S. P. 1298476, 1298477, 1298478, 1298479, 1298480, 1298481, 1919; abst. J. S. C. I. 1919, **38**, 459-A; C. A. 1919, **13**, 1764, 1765. U. S. P. 1303176, 1303177, 1919; abst. J. S. C. I. 1919, **38**, 507-A. E. P. 5156, 1911; abst. J. S. C. I. 1912, **31**, 184. F. P. 344692, 1904; abst. J. S. C. I. 1904, **23**, 1233.

[3] F. Stewart, U. S. P. 811523, 1906; 923088, 1909; 1017023, 1018994, 1912; abst. J. S. C. I. 1906, **25**, 226; 1909, **28**, 737; 1912, **31**, 352; 1913, **32**, 669. In F. P. 465732, 1913; abst. J. S. C. I. 1914, **33**, 589, the raw material is digested with an oxidizing agent, *e. g.*, dilute nitric acid, chromic acid or a mixture of dilute nitric acid and hydrochloric acids under a steam pressure of 4–5 atmos. for 10–30 mins. then drained, washed and neutralized with a 5%–10% solution of sodium hydroxide with which it is boiled for 5–30 mins. The pulp is bleached with ordinary bleach liquor which is gradually brought to the boiling point, a small quantity of dilute nitric acid being then added. The cellular matter of the plants is separated by this process from the fibers and may be collected for use as a filling material.

[4] A. de Vains and J. Peterson, E. P. 19099, 1913; Holl. P. 2395, 1918; abst. C. A. 1915, **9**, 377; 1918, **12**, 2686. U. S. P. 1106994, 1914; abst. J. S. C. I. 1914, **33**, 916. F. P. 449497, 1912; abst. J. S. C. I. 1913, **32**, 482.

drum, for a period of several hours, using concentrated liquors.[1]

In C. Kellner's process,[2] the cellulose material after the soda treatment, is exposed to the action of chlorine and hypochlorous acid, generated at the anode during the electrolysis of brine, the lignocellulose, pectocellulose and other impurities being oxidized and converted into water-soluble or alkali-soluble compounds;[3]

---

[1] F. Kettlebrook, E. P. 3181, 1911; abst. J. S. C. I. 1912, **31**, 225. Compare C. Cross and E. Bevan, E. P. 1548, 1883; abst. J. S. C. I. 1883, **2**, 541. Carpenter and Schulze, D. R. P. 78306; abst. Wag. Jahr. 1895, **41**, 1027; Jahr. Chem. 1895, **48**, 1357; addn. to D. R. P. 71942; abst. Ber. 1896, **28**, 260; Wag. Jahr. 1894, **40**, 1060; Jahr. Chem. 1894, **47**, 1135. C. Clark, D. R. P. 214000; abst. Wag. Jahr. 1909, **55**, II, 506; Chem. Ztg. Rep. 1909, **33**, 597; Zts. ang. Chem. 1909, **22**, 2438. U. S. P. 927950, 927951; abst. J. S. C. I. 1909, **28**, 905; Pap. Fabr. 1909, **8**, 1082; Pap. Ztg. 1909, **34**, 3390.

[2] E. P. 24542, 1902; J. S. C. I. 1903, **22**, 1145. F. P. 326313, 1902; abst. J. S. C. I. 1903, **22**, 817. U. S. P. 773941; abst. J. S. C. I. 1904, **23**, 1159. D. R. Anm. 4724, 1886; Pap. Ztg. 1885, **10**, 233. U. S. P. 542932, 1859. E. P. 4960, 5053, 6951, 6993, 15930, 15931, 1890; 12970, 12971, 1891; abst. J. S. C. I. 1890, **9**, 819; 1891, **10**, 380, 566, 944, 1022. Aust. P. 33685, 56889, 1891. See E. Ritter and C. Kellner, U. S. P. 328812, 329214, 329215, 1885. Aust. P. 20024, 31730. F. P. 157754; abst. Mon. Sci. 1884, **26**, 768. Belg. P. 62746. Ital. P. 16316.

[3] B. Johnsen and R. Hovey, J. S. C. I. 1918, **37**, 132-T; Paper, 1918, **21**, 36; abst. C. A. 1918, **12**, 1250, 1598. In this connection refer to, E. Heuser, Woch. Papierfabr. 1913, **44**, 2209; abst. J. S. C. I. 1913, **32**, 695. E. Heuser and T. Blasweiler, Papier Ztg. 1918, **43**, 593, 613; Chem. Ztg. Rep. 1918, **42**, 108; abst. J. S. C. I. 1918, **37**, 574-A. E. Heuser and A. Haug, Zts. ang. Chem. 1918, **31**, 99, 103, 166, 172; abst. J. S. C. I. 1918, **37**, 365-A, 650-A. See also, J. S. C. I. 1914, **33**, 71. E. Heuser and R. Sieber, Zts. ang. Chem. 1913, **26**, 801; abst. C. A. 1914, **8**, 1343, 2059. E. Heuser and C. Skiöldebrand, Zts. ang. Chem. 1919, **32**, 41; abst. J. S. C. I. 1919, **38**, 215-A. See also, J. S. C. I. 1913, **32**, 822. R. Sieber and L. Walter, Papierfabr. 1913, **11**, 1179; abst. J. S. C. I. 1913, **32**, 974; C. A. 1914, **8**, 1202. A. Schorger, J. Ind. Eng. Chem. 1917, **9**, 556, 561, 748; abst. C. A. 1917, **11**, 2218, 2542; J. S. C. I. 1917, **36**, 867, 1003; Ann. Rep. S. C. I. 1917, **2**, 144. A. Dean and G. Tower, J. Amer. Chem. Soc. 1907, **29**, 1119; abst. J. S. C. I. 1907, **26**, 988. B. Tollens, Zts. ang. Chem. 1898, **11**, 337; abst. J. S. C. I. 1898, **17**, 365, 481, 682. B. Tollens and R. Dmochowski, J. Landwirtschaft, 1910, **58**, 1; abst. Chem. Zentr. 1910, **81**, II, 246. B. Tollens and Krober, J. Landw. 1901, **48**, 357; 1905, **53**, 13. Lange, Zts. physiol. Chem. 1910, **14**, 15, 217. J. Koenig and E. Rump, Unters. Z. Nahr. Genussm. 1914, **28**, 177; abst. C. A. 1915, **9**, 815. H. Wislicenus, Zts. Chem. Ind. Kol. 1910, **6**, 1. H. Wislicenus and M. Kleinstueck, Zts. Chem. Ind. Kolloid, 1910, **6**, 17, 87; abst. J. S. C. I. 1910, **29**, 268. P. Klason, Chem. Ztg. 1903, **27**, 585; abst. J. S. C. I. 1903, **22**, 826. Svensk Pap. Tid. 1916, 129. Papier. Ztg. 1908, **33**, 3779; abst. J. S. C. I. 1908, **27**, 1219; 1909, **28**, 37. Papierfabrikant, 1909, **7**, Fest-und Auslandsheft, 26, 627, 671, 701, 795; abst. J. S. C. I. 1909, **28**, 100. Wochenbl. Papierfabr. 1910, **41**, 464, 541; abst. J. S. C. I. 1908, **27**, 1080; 1910, **29**, 343. Papierfabr. 1910, **8**, 1285; abst. J. S. C. I. 1911, **30**, 79. Pulp and Paper Mag. 1918, **16**, 1015, 1037; abst. J. S. C. I. 1919, **38**, 38-A. See also J. S. C. I. 1916, **35**, 172, 832. P. Klason and H. Mellquist, Papierfabrikant, 1913, **11**, 145; abst. J. S. C. I. 1913, **32**, 227. See also, J. S. C. I. 1910, **29**, 343. P. Klason and B. Segerfelt, Papierfabrikant, 1911, **9**, 1039; abst. J. S. C. I. 1911,

the caustic soda formed at the cathode is utilized for the purification of further quantities of wood. The brine may with advantage be replaced by other chlorides as magnesium chloride.[1]

A very pure cellulose product is obtained from wood pulp which has been purified by the soda process by the following supplementary treatment. The wood pulp is first bleached for several hours with an aqueous solution containing 2%–8% chlorine, the resulting product being then heated under pressure with a solution of sodium carbonate for several hours. The resulting cellulose is washed free from alkali and aerated.[2]

Impurities retained in wood pulp after the soda treatment

30, 1145. R. Benedikt and M. Bamberger, Chem. Ztg. 1891, **15,** 221–222. Compare, Mittheil. k. k. Techn. Gew. Museums, 1888, **18,** 66–67; 1889, 9–14; Jahresber. d. Wiener Handelsak. 1890, 159. J. S. C. I. 1888, **7,** 863–64; 1889, **8,** 574, 735, 925; 1890, **9,** 659, 1156; 1891, **10,** 163, 576. Monatsh. 1890, **11,** 260–67; Chem. Ztg. 1889, **13,** 872, 1087; Monatsh. 1890, **11,** 84; Chem. Centr. 1857, **28,** 321; J. S. C. I. 1890, **9,** 659; 1889, **8,** 735, 925, 1156. J. Koenig, Zts. Unters. Nahr. u Genussm. 1906, **12,** 385; abst. J. S. C. I. 1906, **25,** 1069. Chem. Ztg. 1912, **36,** 1101; abst. J. S. C. I. 1912, **31,** 980. See also J. S. C. I. 1910, **29,** 688; 1912, **31,** 427. J. Koenig and E. Becker, Zts. ang. Chem. 1919, **32,** 155; abst. J. S. C. I. 1919, **38,** 530-A. J. Koenig, J. Hasenbaumer and M. Braun, Zts. ang. Chem. 1913, **26,** 481; abst. J. S. C. I. 1913, **32,** 939.

[1] J. Lifschuetz and Chem. Fab. Gruenau, Landshoff and Mayer, D. R. P. 60233, 69807; abst. Wag. Jahr. 1892, **38,** 1020; 1893, **39,** 427; Ber. 1892, **25,** 298; 1893, **26,** 921; Chem. Centr. 1893, **64,** II, 1015; Zts. ang. Chem. 1892, **5,** 154; 1893, **6,** 465; Jahr. Chem. 1892, **45,** 2899; Meyer Jahr. Chem. 1893, **3,** 366; Chem. Tech. Rep. 1893, **32,** II, 272; Mon. Sci. 1893, **42,** 200.

C. Ellis has described (U. S. P. 1311215) a binder composed of strongly acid sulfite cellulose liquor solids in a non-fluent form, soluble in water, stable on exposure to air while the solids are in the dried condition, and becoming gradually insoluble when subjected to a protracted exposure to air in the presence of moisture. U. S. P. 1311216, a binder, is composed of solid, oxidized constituents of waste sulfite cellulose liquor which has its normal acidity reduced about one-half. U. S. P. 1311217, sulfite cellulose liquor, is partially neutralized, then evaporated to a solid mass and comminuted. U. S. P. 1311218, normally acid sulfite cellulose liquor is treated with a quantity of alkaline substance insufficient to neutralize the liquor, and the product is evaporated by atomizing in the presence of oxygen to form a solid binder. U. S. P. 1311219, an acid binding agent, is prepared by dissolving the desiccated solids of sulfite cellulose liquor in water, the composition being characterized by having a viscosity at least 10% lower than that of ordinary concentrated sulfite cellulose liquor of the same density. U. S. P. 1311220, a dry mixture of acid solids of sulfite waste liquor and lime. U. S. P. 1311211, briquettes or other moulded articles, are made by incorporating atomized, dried, slightly oxidized, water-soluble solids of sulfite cellulose liquor, moulding and converting the solids of the binder into an insoluble form. U. S. P. 1311222, dried, powdered sulfite cellulose liquor solids, are incorporated with an agent capable of rendering them insoluble, a waterproofing agent, water, and a material to serve as a filler, and then shaped.

[2] A. Berglind, E. P. 114456, 1917; abst. J. S. C. I. 1918, **37,** 296-A.

may also be removed by oxidation with a very dilute solution of a manganate or permanganate, the oxidation product being washed out with sulfurous acid.

The alkali remaining after the removal of the wood pulp which has been subjected to the soda treatment, is evaporated in multiple-effect evaporators. The dried residue is ignited and afterwards extracted with water. The aqueous solution of sodium carbonate obtained is treated with lime, and the recovered caustic soda solution employed for the treatment of further quantities of wood. The disposal of the lye may also be carried out thus: The liquid is evaporated to 28°–32° Bé. gravity, the concentrated liquor then passing directly to the so-called "blach-ash furnace," where it is burned with the addition of coal. "Black-ash" results. The hot gases are used to heat the boilers, which provide a portion of the steam for the plants. Sodium carbonate is recovered from the black ash by lixiviation. Acetone can be obtained from the soda lye as follows: The soda liquor to which some extra caustic soda is added, is evaporated to 35° Bé. To 2 tons of this liquor 1 ton of lime is added and a dry, easily handled solid is said to result, but in the writer's experience, it is a very troublesome material to handle. This solid, known by the name of "calignate," is then fed into a horizontal, cylindrical, rotating, retort and subjected to a maximum temperature of 480°, when a destructive distillation occurs. On a manufacturing scale, from 1 ton of waste liquor 24 lbs. of acetone is said to be obtained, in addition to 12 lbs. of methyl alcohol and 6 lbs. of methylethylketone. This process, up to the present time, has not passed beyond the experimental stage.

Sometimes the caustic soda is partly replaced by sodium sulfate and the process is then known as the "sulfate process." The waste lye obtained in the process, when evaporated and ignited, gives in addition to sodium carbonate, considerable amounts of sodium sulfide.

In the preparation of wood pulp by the sulfite process, the wood is heated for several hours at a temperature of 120°–155° with an aqueous solution of sodium, calcium, or magnesium sul-

H. Simpson and G. Mackirdy, E. P. 8817, 1887; abst. J. S. C. I. 1888, **7**, 451. J. VanWessem, E. P. 117086, 1918; abst. J. S. C. I. 1919, **38**, 496-A. R. Pictet and G. Brelaz, D. R. P. 26331, 1883; abst. Wag. Jahr. 1884, **30**, 1147.

fites or a mixture of these salts, the heating being effected by the aid of steam admitted through coils. The digester in which the reaction mixture is contained has a special lining of acid-resisting tile. There are two principal methods in which this digestion is practically carried out.[1] In the R. Mitscherlich process[2] a comparatively low temperature (115°–120°), and a pressure of 2.5–4 atmospheres, is employed. The time of heating is 24–48 hours, and a strong fiber cellulose is obtained. In the Ritter-Kellner process the temperature is raised to 140°–155°, the heating being preferably carried out with live steam for a period of 8–16 hours (pressure 4–6 atmospheres). In the initial stages of the heating in both processes when the temperature is about 70°, the digester is opened for a short period to allow air expelled from the pores of the wood to escape.[3] During the pressure-boils, the non-cellulose constituents of the wood are attacked, and are converted into soluble products.

The preparation of alkali sulfite on a large scale is carried out as follows: A tower about 60 feet high and 6 feet diameter is divided into about 30 sections by means of gratings. These segmental compartments are packed with limestone or magnesite. A battery of such towers is usually erected. From the top, water flows slowly down the tower, sulfur dioxide enters at the bottom and is forced upwards. A portion of the sulfur dioxide is absorbed by the water but the exit gases from the top of the tower still contain sulfur dioxide, and this gas is led to the base of a second tower and the process repeated. The sulfur dioxide dissolves in the water to sulfurous acid, which then attacks the limestone or magnesite and the corresponding sulfite is formed.

Instead of using limestone or other mineral packed in a tower, a liquid or an emulsion may be employed. In a recent

[1] J. Beveridge, J. S. C. I. 1916, **35**, 563; abst. C. A. 1916, **10**, 2799. E. P. 2872, 1891; 14105, 1892; abst. J. S. C. I. 1892, **11**, 176; 1893, **12**, 779. For cymene production from sulfite cellulose, see T. Ortenblad, Teknisk Tidsk. 1918, **8**; Papierfabr. 1918, **16**, 717; C. A. 1919, **13**, 2276.

[2] D. R. P. 4178, 4179, 1878; abst. Dingl. Poly. 1883, **249**, 23. E. P. 11816, 1884; abst. J. S. C. I. 1885, **4**, 549; Dingl. Poly. 1876, **220**, 479; abst. Chem. Tech. Mitth. 1875, 255; Dingl. Poly. 1884, **251**, 262. U. S. P. 284319, 1883; abst. Dingl. Poly. 1884, **251**, 262; Papier Ztg. 1884, 1. See A. Tilgham, E. P. 385, 1867; 2924, 1886. U. S. P. 70485, 1867; 92229, 1869.

[3] C. Schwalbe, Wochbl. Papierfabr. **44**, 2786; Papierfabr. **11**, 1095; abst. C. A. 1914, **8**, 245. F. Cohn, Pap. Ztg. 1884, **9**, 1929. M. Coulon and R. Godeffroy, D. R. P. 88299; abst. Ber. 1896, **29**, 888; Wag. Jahr. 1896, **42**, 1027. S. Ferenczi, Pap. Ztg. 1897, **22**, 3575, 3647, 3679.

patent[1] is described an apparatus in which milk of lime is placed in a tower or vessel divided vertically into a series of compartments with connecting tubes between the divisions for the passage of sulfur dioxide. C. Schwalbe[2] disintegrates the wood with calcium sulfite lye without heating under pressure. The wood is soaked for 3–5 hours at 70°–100° in a solution of calcium sulfite containing about 3% by weight of SO_2. The lye is then drawn off and gaseous sulfur dioxide injected until the acid content in the wood is doubled. The lye still present is then washed out and the material steamed.

With ammonium sulfite lyes containing excess of free ammonia a higher pressure can be developed than with soda lyes.[3] The ammonium sulfite lye may be regenerated by driving off the free ammonia, collecting the condensate in water, and treating this with sulfurous acid. For the treatment of pine wood a satisfactory composition of lye is:—3%–3.5% sulfur dioxide and 1.7%–2% ammonia. The wood is digested for ten hours at a temperature of 165° at a pressure of 10–12 atmospheres. A yield of 65% unbleached cellulose from the pine wood is claimed by operating in this manner.

C. Harnist[4] treats the crude cellulose successively or alternately with ammonia (or other alkaline solution) and sulfur di-

---

1. A/S Themes Mek. Voerkstad, Norw. P. 27202, 1916; abst. C. A. 1916, **10,** 3141. For methods of determining the purity of wood cellulose, consult, E. Richter, Wochbl. Papierfabr. 1912, **43,** 1631; 1913, **44,** 1776; abst. C. A. 1912, **6,** 2524; J. S. C. I. 1912, **31,** 530; 1913, **32,** 594. Eighth Int. Cong. Appl. Chem. 1912, **13,** 233; abst. J. S. C. I. 1912, **31,** 530, 869.

2. D. R. P. 282050, 1913; abst. C. A. 1915, **9,** 2312; abst. Chem. Zentr. 1915, **86,** I, 411; Chem. Ztg. Rep. 1915, **39,** 77; Zts. ang. Chem. 1915, **28,** 224. H. Fleck, Pap. Ztg. 1884, **9,** 1804. R. Gans, E. Stone and B. Tollens, Ber. 1888, **21,** 2148; abst. J. C. S. 1888, **54,** 1059; J. S. C. I. 1888, **7,** 595; Bull. Soc. Chim. 1889, **1,** 746; Jahr. Chem. 1888, **41,** 2309. For method of manufacture of wood pulp from California "Redwood" tree, see E. P. 8817, 1887.

3. J. and A. Rosenblum, G. de Gottinan, L. Brech and E. Tyborowski, E. P. 5552, 1911; abst. J. S. C. I. 1912, **31,** 329; C. A. 1912, **6,** 2529. F. P. 460472, 1913; abst. J. S. C. I. 1914, **33,** 19. A. de Vains and J. Peterson, E. P. 19099, 1913; abst. J. S. C. I. 1914, **33,** 746. F. P. 449497, 1912; abst. J. S. C. I. 1913, **32,** 482.

4. F. P. 477895, 1914; abst. C. A. 1916, **10,** 1433. A. Gawalowski, Pap. Ztg. 1899, **24,** 3112. R. Gentzen and L. Roth, D. R. P. 147844, 1901; abst. Wag. Jahr. 1904, **50,** II, 370; Chem. Centr. 1904, **75,** I, 410; Chem. Ztg. 1904, **28,** 66; Zts. ang. Chem. 1904, **17,** 244; Jahr. Chem. 1904, **57,** 878; Chem. Ztg. 1904, **28,** 66. J. Lifschuetz, D. R. P. 60233; abst. Ber. 1892, **25,** 298; Chem. Centr. 1893, 64, II, 1015; Zts. ang. Chem. 1892, **5,** 154; Jahr. Chem. 1893, **3,** 366.

oxide. Compressed or liquefied ammonia and sulfur dioxide can also be used.

Purified cellulose fiber can also be obtained from wood chips[1] by boiling under pressure with water in presence of 10% calcium oxide and 2%–4% of finely divided sulfur. The chips are washed and disintegrated or partly separated into a fibrous condition by means of a beating machine or hollander, subsequent boiling with soda ash eliminating the sulfur. This treatment is followed by washing and drying. The resulting fiber still contains 0.3%–0.4% of sulfur.

J. Hasenbaumer[2] claims that a very pure cellulose may be obtained from fir, pine and beech by a combination of the alkali and sulfite processes, on account of the fact that the resulting mother liquors are more readily utilized. By the action of dilute alkali followed by that of dilute acid the advantages of both the soda and sulfite treatments are obtained. The resulting lye is free from large excess of soda or sulfite and it is claimed can be utilized as a fodder.[3] The wood is digested for 5–6 hours at 2–3 atmospheres pressure with 4–5 times its volume of aqueous ammonia (concentration 3%–5%), or soda (concentration 1%–2%). When ammonia is used it is recovered from the waste lye. In this process 3%–5% of resin and 1%–2% of tannic acid are recovered from coniferous wood. The wood residue is then digested for 6–8 hours at 1–2 atmospheres pressure with five times its volume of dilute sulfuric acid (concentration about 0.5%). The hemi-celluloses are dissolved and the residual lye contains considerable amounts of sugar. This mother liquor is mixed with the liquors from the alkaline digest and the mixture poured over hay or ab-

1. V. Drewsen, U. S. P. 996225; abst. C. A. 1912, **6,** 2315; J. S. C. I. 1911, **30,** 950. E. P. 5157, 1911; abst. J. S. C. I. 1912, **31,** 184. D. R. P. 67889; abst. Wag. Jahr. 1893, **39,** 1060; Ber. 1893, **26,** 559. E. Goldschmidt, D. R. P. 97935, 1897; Chem. Centr. 1898, **69,** II, 616; Pap. Ztg. 1898, **23,** 2664. L. Gottstein, Wochenbl. Pap. 1905, **36,** 1390, 1616, 1779; Zts. ang. Chem. 1905, **18,** 983. C. Grabowski, Aust. P. 44713, 1894.

2. J. Hasenbäumer, M. Braun and J. Hoenig, Zts. ang. Chem. 1913, **26,** 481; abst. C. A. 1914, **8,** 420. E. Kirchner, Das Papier, 1907, **3,** 615; Wochenbl. Papierfabr. 1904, **35,** 3411; 1910, **41,** 1995; abst. J. S. C. I. 1904, **35,** 3411; 1910, **29,** 873. A. Frank, Papier Ztg. 1896, **21,** 354; abst. J. S. C. I. 1896, **15,** 370; Papier Ztg. 1913, **38,** 136. E. P. 13286, 1886; abst. J. S. C. I. 1887, **6,** 735.

3. J. Koenig, Zts. Nahr. Genussm. 1916, **31,** 171; abst. J. S. C. I. 1916, **35,** 960. A. Harpf, Pap. Ztg. 1891, **16,** 1726, 1788, 1844, 1908, 1964, 2026, 2094, 2155; 1892, **17,** 792, 1089, 1121, 1525, 1557, 1643; Zts. ang. Chem. 1898, **11,** 875, 925, 1169; Chem. Centr. 1899, **70,** I, 313.

sorbed by dry grain. When lime, followed by sulfuric acid is used, the insoluble gypsum formed has no injurous action in the fodder mixture. When soda is used it is necessary to follow up with hydrochloric acid in the acid treatment, and the resulting sodium chloride does not reduce the food value of the fodder. The lignin which still remains in the cellulose is removed by oxidizing with a bleaching agent. If spinning fibers are required, the strength of the reagents and the pressure and time of the alkali and acid boils are diminished.

Many suggestions have been put forward for the utilization of the aqueous lye from the sulfite process,[1] but hitherto there has been but little success in this direction. During the sulfite treatment, 45%–55% of the wood is converted into soluble constituents. The spent sulfite lye containing the soluble material from the wood has hitherto been mainly regarded as a waste product, and allowed, after neutralization, to flow away.

According to analyses by H. Seidel of the Ritter-Kellner waste liquors, the latter average 11.4% solids. The dried residue obtained on evaporation has the approximate ash-free composition of—carbon = 53.7%, hydrogen = 5.2%, sulfur = 8.8% and oxygen = 32.3%. A more detailed analysis of various waste liquors has been given by C. Hoffmann.[2]

TABLE XXX.—ANALYSIS OF WASTE SULFITE LIQUOR

	Grams per Liter				
	1	2	3	4	5
Total solids	82	88	85	93	92
Loss on ignition	68	75	...	81	....
Ash	14	13	16	12	....
Total sulfur	....	....	....	....	9.2
Free sulfur dioxide	2.6	2.2	2.9	2.6	3.8
Sulfite radical (SO_3)	7.3	7.9	6.7	1.2	3.8
Sulfate radical (SO_4)	4.1	5.4	4.8	2.7	1.9
Oxygen consumed	52	52	50	60	....

---

1. H. Seidel and L. Hanak, Mitt. d. k. k. Tech. Gew. Mus. N. F. 1897, **7**, 119, 283; 1898, 368; Rev. Gen. Mat. Color. **2**, 370; abst. J. S. C. I. 1898, **17**, 178, 596, 844, 863, 1043; 1900, **19**, 1033; Chem. Centr. 1899, **70**, I, 312; Zts. ang. Chem. 1898, **11**, 1054; Pap. Ztg. 1898, **23**, 75. H. Seidel, D. R. P. 99682, 1897; Zts. ang. Chem. 1900, **13**, 951, 1307; Pap. Ztg. 1900, **25**, 3295, 3371; J. S. C. I. 1900, **19**, 1033. See also Dissertation, Goettingen, 1892. J. Lindsey and B. Tollens, Ann. 1891, **267**, 341; abst. Ber. 1892, **25**, 322; Zts. ang. Chem. 1892, **5**, 154. A. Pictet, E. P. 121723, 1918; abst. J. S. C. I. 1919, **38**, 298-A.

2. "Praktische Handbuch der Papier Fabrikation," 1897. C. Hoff-

The sulfite lye usually has a specific gravity of about 1.05 and contains considerable quantities of the deliquescent calcium salt of lignonsulfonic acid.[1] In addition, there is present sugar, resins, tannins, gummy matter, xylone and some volatile acids (mainly acetic). The sugar content of the waste liquor before evaporation averages 1%–2.5%, about 70% of which is dextrose, the remainder being mainly mannose and galactose. As a general rule, the higher the temperature during the digestion of the wood with the bisulfite, the greater the amount of sugar formed.[2] To obtain alcohol[3] from this liquid it is first freed from fatty acids and sulfur dioxide by vacuum distillation, although this is not essential. This distillation may be carried out on the residual waste liquors or may be previously done during the digestion of the wood.[4] The waste liquor is next neutralized with lime, the precipitated calcium salts and parts of the organic matter removed by filtration, and the filtered liquid treated with a special yeast cultivated for the purpose, the solution meanwhile being aerated.

---

mann, Pap. Ztg. 1896, **21**, 2483. D. R. P. 128213 is by M. Hoffmann, Papier Ztg. 1902, **27**, 817; 1905, **30**, 3374; abst. J. S. C. I. 1902, **21**, 502; 1905, **24**, 1250. A. Staempfli, D. R. P. 309969, 1918; abst. J. S. C. I. 1919, **38**, 283-A.

[1] M. Hoenig and J. Spitzer, Monatsh. Chem. 1918, **39**, 1; abst. J. S. C. I. 1918, **37**, 502-A. E. Hoehn, Pap. Ztg. 1887, **12**, 245. J. Juergensen, D. R. P. 73718, 1892; Ber. 1894, **27**, 445; Wag. Jahr. 1894, **40**, 50; Chem. Centr. 1894, **65**, I, 1168; Zts. ang. Chem. 1894, **7**, 188; Jahr. Chem. 1894, **47**, 1136. Gore, Pap. Ztg. 1903, **28**, 1282; Dingl. Poly. 1907, **322**, 427. Oesterreichische Ver. Chemische u Metallurgische Produktion, D. R. P. 25485, 1882; abst. Wag. Jahr. 1884, **30**, 1151.

[2] E. Simonsen, Norsk. teknisk Tids. 1895, 65; abst. J. C. S. 1896, **70**, i, 331. W. Kerp and P. Woehler, Pap. Fab. 1909, **7**, 45, 1131; Pap. Ztg. 1909, **34**, 3286; 1910, **35**, 1932; Chem. Centr. 1909, **80**, II, 710. A. Klein, Zts. ang. Chem. 1907, **20**, 610; Pap. Ztg. 1905, **30**, 3955; 1906, **31**, 167, 474, 4286; Wochenbl. Papierfabr. 1909, **40**, 240; Chem. Ztg. 1906, **30**, 1259.

[3] T. Koerner, Zts. ang. Chem. 1908, **21**, 2353; abst. J. C. S. 1908, **94**, i, 955; J. S. C. I. 1908, **27**, 1216. See also E. Simonsen, J. S. C. I. 1898, **17**, 365, 481, 1164. A. Classen, J. S. C. I. 1900, **19**, 1028. P. Nicolardot, F. P. 476696, 1914; abst. J. S. C. I. 1916, **35**, 613. In the treatment of sawdust, or other material containing cellulose with the object of producing alcohol and organic by-products, the vapors which escape when the digesters are opened are condensed in contact with alkaline-earth carbonates, which retain the acids but allow aldehydes, etc., to pass. The large proportion of organic acids remaining in the liquor in the digesters, which hinders the fermentation of the dextrose, is almost entirely removed by vacuum distillation. The acid vapors are absorbed in milk of lime in large receivers acting as vacuum accumulators.

[4] A. and E. Lederer, F. P. 464608, 1913; abst. J. S. C. I. 1914, **33**, 478. B. Newlands, E. P. 16510, 1906; abst. J. S. C. I. 1907, **26**, 835; C. A. 1907, **1**, 2515. H. Krause, Chem. Ind. 1906, **29**, 217; abst. Chem. Centr. 1906, **77**, I, 1851; J. S. C. I. 1906, **25**, 493. K. Kraut, Pap. Ztg. 1886, **11**, 1419.

The fermentation takes about five days, the alcohol formed is separated by distillation. It is claimed that this process of producing alcohol is very cheap and can rival the production of alcohol from food products. As the fermentable sugar content of the waste lye is small, the production of alcohol, therefore, does not solve the problem of the utilization of the sulfite lye.

H. Seidel proposes the use of waste sulfite liquor, under the name of lignorosin, as an assistant in mordanting wool with bichromate, to replace tartar emetic or lactic acid.

As to its use as a reducing agent the following example may be cited: 10 grams 1.1-di-nitronaphthalene, 800 cc. water, 20 cc. waste sulfite lye, 20 gm. sodium bisulfite, 38° Bé., and 20 gm. soda lye, 30° Bé. are heated on a water bath until complete solution results. The greenish blue solution obtained is acidified with hydrochloric acid and boiled until free from sulfur dioxide. The dyestuff is then precipitated with alcohol. It dyes wool dark violet and silk violet-grey from an acid bath. The reducing power of the sulfite liquor renders the color somewhat fugitive.

Waste sulfite lye may be employed in the indigo vat. The following directions give the method of working according to H. Seidel and L. Hanak: 2283 kilos indigo 80% (ground with soda lye—1 part indigo, 3 parts water), 3.75 kilos slaked lime, 2.5 kilos calcined soda, and 10 kilos sulfite liquor 28° Bé. are brought to 62.5 liters with water and heated with direct steam until a reaction suddenly begins at 75°. The vat is then made up to 500 liters and the diluted liquid treated with 10 kilos sulfite lye, 3.75 kilos lime and 2.5 kilos of calcined soda. The subsequent working is the same as when glucose is employed. The sulfur content of the evaporated lye is but 6%–8% and mainly present in organic combination. It is difficult to recover this sulfur economically. It has also been proposed to recover the sodium salts.[1]

In V. Drewsen's method[2] the waste sulfite lye is heated with

---

[1] E. Rinman, Swed. P. 33084, 1910; abst. C. A. 1913, **7**, 700. U. S. P. 1017320, 1912; abst. J. S. C. I. 1912, **31**, 279. U. S. P. 1202317, 1916; abst. J. S. C. I. 1916, **35**, 1215. D. R. P. 285752, 1914; abst. J. S. C. I. 1915, **34**, 1139. Ver. Zellstoff u Papierchem. Dec. 5, 1914; abst. Chem. Ztg. 1915, **39**, 99; abst. J. S. C. I. 1915, **34**, 274. See also J. S. C. I. 1912, **31**, 274.

[2] V. Drewsen, D. R. P. 67889, 1891; Ber. 1893, **26**, 558; Pap. Ztg. 1893, **18**, 1280. V. Drewsen and L. Dorenfeldt, U. S. P. 620751, 726036, 1899; Chem. Ztg. 1899, **23**, 276. K. Lehmann, Pap. Ztg. 1893, **18**, 1924, 1956, 1989, 2025, 2057, 2089, 2122, 2153.

caustic lime under a pressure of six atmospheres. The calcium mono-sulfite formed in the reaction is converted into the soluble bisulfite compound by means of sulfurous acid. The cost of this process, however, is said to be high.

When the sulfite lye, as separated from the cellulose material, cannot be utilized in this condition or when it is inconvenient to run large amounts of it to waste, then the only alternative is to evaporate the liquid, the evaporation being preferably carried out in vacuo. When the moisture content of the residue is about 50%, the material may be used as a fuel direct; it is then subjected to dry distillation, with recovery of good charcoal from the retort and of organic products from the distillate. The residual material in the evaporation may, on the other hand, be mixed with an equal weight of sawdust and made into briquettes.[1] This fuel has a calorific value of about 60% of that of an average coal.[2] H. Seidel neutralizes the sulfite liquor with lime, saturates the solution with carbon dioxide and then concentrates in vacuum evaporators or in a multiple-effect apparatus.

The evaporated material is of a gummy nature (owing to the presence of calcium salts of the lignonsulfonates) and contains only relatively small quantities of nitrogen, potash or phosphate, and therefore is unsuitable as a manure from the standpoint of fertilizing efficiency. Owing to the gummy and plastic nature of the material, it has been utilized as a substitute for resins and gums. It is also a possible sizing material, but with only limited application in this direction. The material may be used as a source of oxalic acid but its employment is met by the competition from sawdust, which yields oxalic acid more economically.

Owing to the great bulk of water (90%) present, it is expensive to obtain the solid residue by evaporation. A process has been developed by E. Oman in which the expense of removing the water, in cold countries such as Sweden, may be reduced by

---

[1] R. Strehlenert, Chem. Trade J.; J. Ind. Eng. Chem. 1916, **8**, 1070. Can. P. 190864, 1919; abst. C. A. 1919, **13**, 1764. Papierfabr. 1913, **11**, 645, 666; abst. J. S. C. I. 1913, **32**, 652. See "Literature of Sulfite-cellulose Spent Liquors," M. Mueller, Berlin, 1911, 114 pages.

[2] Engineering, 1916, 177. A. Leonhardt, D. R. P. 34420, 1885; abst. Wag. Jahr. 1885, **31**, 1043; 1886, **32**, 938. C. Liesenberg, D. R. P. 37882, 1886; abst. Wag. Jahr. 1888, **34**, 1178; Chem. Centr. 1887, **58**, 132; Pap. Ztg. 1887, **12**, 398.

40%. This is brought about by freezing out the water. In this way four-fifths of the total water can be readily removed and the residue worked up for organic constituents. A method of recovering lignon sulfonates by salting out has also been proposed by E. Oman.[1]

Another possible use of spent sulfite lye is in connection with the leather industry. Hide powder will absorb about 20% of dry sulfite residue.[2] In W. Dickerson's patent[3] waste sulfite lye is used for the manufacture of a tanning extract. The lye is digested with an electrolyte such as sodium chloride, which is capable of gelatinizing the liquid or of converting it into a mobile fluid when concentrated. Treatment of the lye with 1% of benzoyl chloride in a weak alkaline solution is said to separate the tannins in the form of a white powder.

The soda and sulfite treatments give a wood pulp suitable for most purposes, especially if a bleaching treatment has been carried out. The average composition of the purified wood pulp prepared by the various chemical methods is approximately the same, being carbon 50%, nitrogen 6% and oxygen 44%. The wood pulp is, for example, suitable for paper manufacture and it may be used as an absorbent of nitroglycerol in the preparation of gelignite.[4] If required, however, for the preparation of yarn,

---

[1] E. P. 103479, 103480, 103822, 1917; abst. J. S. C. I. 1918, **37**, 407-A, 541-A, 573-A. E. P. 103649, 103650, 103651, 103652, 103653, 103654, 103655, 1917; abst. C. A. 1917, **11**, 1749; J. S. C. I. 1918, **37**, 121 A, 146 A, 461 A. U. S. P. 1130192, 1915; abst. J. S. C. I. 1915, **34**, 419. E. P. 1145, 1914; abst. J. S. C. I. 1914, **33**, 348. F. P. 467466, 1914; abst. J. S. C. I. 1914, **33**, 828. Chemikerversammlung, Stockholm, May 28–29, 1915; Chem. Ztg. 1915, **39**, 820; abst. J. S. C. I. 1916, **35**, 172.

[2] See D. R. P. 75351; abst. Wag. Jahr. 1894, **40**, 1061; 86651; abst. Zts. ang. Chem. 1896, **9**, 343; 93944; 93945, abst. Wag. Jahr. 1897, **44**, 1066, 1067; 122489; abst. Zts. ang. Chem. 1901, **14**, 808; 183415; abst. Wag. Jahr. 1907, **53**, II, 503; 194872; abst. Wag. Jahr. 1908, **54**, II, 487. J. Graham, E. P. 5365, 5366, 5367, 5368, 1882. D. R. P. 23718, 1882; abst. Dingl. Poly. 1884, **251**, 70; Papier Ztg. 1883, 434; Wag. Jahr. 1884, **30**, 247.

[3] U. S. P. 1043303, 1912; abst. J. S. C. I. 1912, **31**, 1160. C. Meyer, Aust. P. 1210, 1889. E. Morterud, Wochenbl. Papierfabr. 1907, **38**, 1056 Pap. Ztg. 1906, **31**, 3819; 1907, **32**, 296.

[4] Here it serves the double purpose of absorbing the nitroglycerol and reducing the temperature of explosion. It should be free from acid and foreign substances, especially metallic particles, and should contain but little resin. The moisture should be under 10%, and should absorb nitroglycerol readily. For the preparation of adhesives from sulfite liquor, see E. P. 2924, 1866; 6652, 1912; 304, 1913. For cellulose briquettes, compare Belg. P. 133967, 1898; 254944, 1913. The J. Jurgens and H. Timpe plastic of cellulose and aluminates is described in Belg. P. 228578, 1910.

nitrocellulose, cellulose xanthate, various plastic films of artificial silk, further purification is expedient, as there are impurities present which impair its use in the preparation of these products.[1]

To take a particular example, wood-cellulose from the sulfite process, gives a lower yield on nitration, as compared with the yield from purified cotton. The nitration product also has a lower ignition temperature and a greater solubility in ether-alcohol.[2] According to Klemm, one of the chief difficulties in obtaining uniformity from wood cellulose, lies in the different structures of the cells of the spring and autumn growths, and it is suggested that wood grown in tropical regions would afford more uniform results under chemical treatment.

Wood pulp is composed of cellulose of varying degrees of purity, together with some incrusting matter, resins, gums and

---

1. E. Opfermann, E. Friedmann and Akt. Ges. f. Maschinenpapierfabrikation, D. R. P. 219085, 1910; abst. Wag. Jahr. 1910, **56**, II, 427; Chem. Zentr. 1910, **81**, I, 978; Chem. Tech. Rep. 1910, **34**, 135; Chem. Ind. 1910, **33**, 154; Chem. Zts. 1910, **9**, 2031; C. A. 1910, **4**, 2044; Jahr. Chem. 1910, **63**, 429. F. P. 402462, 1909; abst. J. S. C. I. 1909, **28**, 1270. E. Schauffelberger, U. S. P. 1282635, 1917; abst. J. S. C. I. 1919, **38**, 9-A. E. P. 113494, 1917; 124676, 1918; abst. J. S. C. I. 1918, **37**, 2033; 1919, **38**, 357-A. Can. P. 187949, 1918; abst. C. A. 1919, **13**, 1149. F. P. 402462, 1909; abst. J. S. C. I. 1909, **28**, 1270; Mon. Sci. 1911, **74**, 154. E. P. 10604, 1909; abst. J. S. C. I. 1910, **29**, 269.

2. K. Nitzelnadel (Wochbl. Papierfabr. 1912, **43**, 3488; abst. J. S. C. I. 1912, **31**, 954; C. A. 1913, **7**, 257) has prepared nitrocellulose from various samples of sulfite wood pulp, bleached and unbleached, also from straw cellulose. These materials contain higher proportions of non-cellulose impurities than the cotton ordinarily employed in the nitrocellulose industry; straw pulp also possesses the disadvantage of not being readily wetted by liquids. The nitration experiments showed that sulfite wood pulp yields products containing at least as much N as those prepared from cotton; the products from straw cellulose were generally rather poorer in N. The solubility in ether-alcohol of the nitrocellulose prepared from these celluloses was generally over 40%; in one case only was it as low as 13%. The films obtained on evaporating the solutions were inferior to those from solutions of nitrated cotton. The stability tests, performed according to Will's method, showed that these nitrocelluloses were sufficiently stable to satisfy official specifications; the products from straw cellulose showed the lowest stability. The ignition temperature, according to Kast's test, was in general somewhat lower than for nitrated cotton, but all the nitrocelluloses prepared from wood fiber showed temperatures of ignition well above the specified minimum limit of 180°; the products from straw cellulose tended to fall below this limit. The yields of nitrocellulose from sulfite wood pulp were lower than those obtained from cotton; straw cellulose gave the lowest yields. His conclusions are in favor of the use of wood cellulose as a raw material in the nitrocellulose industries, but considers straw cellulose unsuitable. The disadvantages of wood cellulose, as compared with cotton, are the lower yields, the lower ignition temperature of the products, and the greater solubility in ether-alcohol.

quinoline-like compounds.[1] A process has been patented to improve the wood pulp so as to make it more suitable for special purposes, as for the preparation of highly nitrated gun-cotton.[2] The wood cellulose is freed from incrusting matter by further chemical treatment using any of the known processes. The material is then reduced to a high degree of mechanical division in a special disintegrator. The chemical action must not be too drastic or the cellulose itself may be attacked. If the latter occurs appreciable amounts of oxycellulose are formed during the subsequent bleaching operations. In such cases, where oxycellulose is present it is difficult to obtain a stable highly nitrated cellulose. In addition, the solutions made for the production of artificial filaments have too low a viscosity and are also unsuitable for artificial filament formation.[3] Overbleached cellulose can be detected by its reducing action, the reducing power being expressed in the so-called copper number, and for a cellulose to be suitable for nitration the copper number must be low. Absolutely pure cellulose has no reducing power.[4] The risk of ob-

---

1. R. Sieber, Paper, 1915, **16,** 13; abst. C. A. 1915, **9,** 3128. Schriften des Vereins der Zellstoff-u. Papierchem. **9,** Zts. ang. Chem. 1916, **29,** R, 429; abst. J. S. C. I. 1916, **35,** 1151. See also J. S. C. I. 1909, **28,** 438.

2. Zellstoff-fabrik Waldhof, (E. P. 336, 1891; abst. J. S. C. I. 1892, **11,** 180; Mon. Sci. 1892, **40,** 166). This process seeks to obviate the lack of uniformity which wood pulp often has, and at the same time to remove all incrusting and extraneous material. This is accomplished by chemical treatment, aided by a high degree of mechanical subdivision of the purified pulp, the latter being accomplished by means of a disintegrating apparatus on the order of a carding or tearing machine. The disintegrator consists of two rings or discs carried on separate shafts placed in line with one another and rotating in opposite directions at a speed of about 1500 revolutions per minute. These discs carry pins so adjusted that the pins on one disc pass between the pins of the other, the cellulose being introduced through a central orifice in one of the discs is centrifugally thrown, and thus becomes uniformly comminuted. The material is passed through the machine a sufficient number of times, until a sample, after nitrating, washing and drying, has the requisite fineness.

3. C. Piest, Zts. ang. Chem. 1913, **26,** 24; abst. Kunst. 1913, **3,** 92; C. A. 1913, **7,** 1284; Papierfabr. 1914, **12,** 860; J. S. C. I. 1914, **33,** 856. Mountsing, D. R. P. 189735; abst. Wag. Jahr. 1907, **53,** II, 499; Chem. Ztg. Rep. 1907, **31,** 536; Zts. ang. Chem. 1908, **21,** 270. F. Muellner et al., D. R. P. 96467, 1897; Pap. Ztg. 1898, **23,** 687; 1062, 1218; abst. Wag. Jahr. 1898, **44,** 1108; Chem. Zentr. 1898, **69,** I, 1183; Chem. Ztg. 1898, **22,** 300; Zts. ang. Chem. 1898, **11,** 378; Jahr. Chem. 1898, **51,** 398, 1373. See A. Mitscherlich, E. P. 12927, 1893; abst. J. S. C. I. 1894, **13,** 834. C. Ekman, E. P. 20036, 1893; abst. J. S. C. I. 1894, **13,** 1085. Zellstofffabrik Waldhof and V. Hottenroth, Swiss. P. 77322, 1918; abst. C. A. 1918, **12,** 2248; addn. to Swiss P. 76329; abst. C. A. 1918, **12,** 1123.

4. C. Schwalbe, Ber. 1907, **40,** 1347; abst. Chem. Centr. 1907, **78,** I, 1490; Chem. Ztg. Rep. 1907, **31,** 302; C. A. 1907, **1,** 1696, 2179; J. C. S.

taining oxycellulose can be considerably reduced by employing alkali carbonate instead of caustic alkali, and alkali sulfite in the final purification process. In addition, a less drastic bleaching is required. A suitable concentration of lye is 0.5% to 2% with a boiling of 3–6 hours at a pressure of 2–3 atmospheres.[1]

An impurity usually present in wood pulp prepared by the ordinary chemical methods is a small quantity of resin, pitch and oily matter. The resin content is usually less in bleached than in unbleached wood pulp. The soda process, on account of the more drastic chemical action, gives a purer product from the point of view of resin content than sulfite wood pulp, the resin in the former type being but 0.05%. In the R. Mitscherlich process[2]

1907, **92**, i, 390; J. S. C. I. 1907, **26**, 548; Jahr. Chem. 1905–1908, II, 961; Zts. ang. Chem. 1908, **21**, 265. M. Mueller and E. Meyer, D. R. P. 112449; abst. Wag. Jahr. 1900, **46**, II, 529; Chem. Centr. 1900, **71**, II, 827; Chem. Ztg. 1900, **24**, 674; Dingl. Poly. 1902, **317**, 750. A. Nettl, Aust. P. 1576, 1888. Compare W. Normann, Chem. Ztg. 1906, **30**, 584; abst. Chem. Centr. 1906, **77**, II, 719; Zts. ang. Chem. 1906, **19**, 993; abst. Chem. Centr. 1906, **77**, II, 673.

[1] Refer to "Alcohol from Wood Waste," U. S. Consulate Report, Nov. 1911; abst. J. S. C. I. 1911, **30**, 1466. F. Raschig (E. P. 11568, 29696, 1912. F. P. 441419, 1912; abst. J. S. C. I. 1912, **31**, 845; 1913, **32**, 254. abst. J. S. C. I. 1913, **32**, 454) prepares potassium, sodium and ammonium; nitrate explosives by adding thereto the dry residue from the lyes obtained in the manufacture of cellulose by the sulfite process. D. Newbaecker, D. R. P. 110972, 1899; abst. Wag. Jahr. 1900, **46**, II, 315; Chem. Ztg. 1900, **24**, 570; Zts. ang. Chem. 1900, **13**, 674; Chem. Zts. 1902, **1**, 191. J. Novak, D. R. P. 74030, 1893; Ber. 1894, **27**, 474; Pap. Ztg. 1894, **19**, 1169; Wag. Jahr. 1894, **40**, 1061.

[2] W. Herzberg, Papier Ztg. 1906, **31**, 3819; Mitt. Materialprüfungsamt. **22**, 180; abst. Chem. Centr. 1905, **76**, I, 1286; Mitt. Koenig. tech. Versuchs, 1890, **13**, 132; abst. 1904, **22**, 180; abst. J. S. C. I. 1890, **9**, 112, 1068; 1891, **10**, 661; 1897, **16**, 350; 1901, **20**, 739; 1905, **24**, 453. Papierfabr. 1911, **9**, 914, 948; abst. J. S. C. I. 1911, **30**, 1049. See also Sitz. d. poly. Gesellsch. Berlin, 1882; Papier Ztg. 1884, 432; Ber. 1887, **20**, 808; J. S. C. I. 1887, 565; 1891, **10**, 576. A. Mitscherlich, D. R. P. 4178, 4179, 1878. E. P. 1548, 1883; Ber. 1879, **12**, 395; Papier Ztg. 1883, **8**, 343, 718, 750, 824, 893, 932, 934, 999, 1029, 1425, 1469, 1498, 1529, 1633, 1670, 1705; 1884, **9**, 213, 249, 285, 1715, 1763, 1801. It should be noted that D. R. P. 4178 is identical with Sachs, D. R. P. 3912, 1875. D. R. P. 34420, 1885; 54206, 1890; 72161, 1891; 72362, 1891; 82498, 1893; 86651, 1895; 93944, 1896; abst. Ber. 1891, **24**, 343; 1894, **27**, 149, 221; 1895, **28**, 869; 1897, **29**, 452; Pap. Ztg. 1893, **18**, 3222; 1894, **19**, 272; 1895, **20**, 2716; 1896, **21**, 1848; 1897, **22**, 3074, 3148. D. R. P. 169408, 169409, 1903; abst. Wag. Jahr. 1906, **52**, II, 546; Chem. Ztg. 1906, **30**, 489; Zts. ang. Chem. 1907, **20**, 368. D. R. P. 220066, 1908; abst. Pap. Ztg. 1906, **31**, 1732; 1893, **18**, 1673; 1896, **21**, 2344, 2850; Wag. Jahr. 1910, **56**, II, 527; Chem. Zentr. 1910, **81**, I, 1309; Chem. Ztg. Rep. 1910, **34**, 180; Zts. ang. Chem. 1910, **23**, 959. Aust. P. 112, 1894; 2945, 1897. For history of work of Mitscherlich, see Paper, 1916, **18**, No. 18, p. 17. In this connection compare R. Kuhn, Pap. Ztg. 1895, **20**, 120, 248, 466, 500, 562, 663, 727, 822, 952, 983, 1083, 1147, 1351, 1445, 1547, 1870.

the resin is usually 0.3%–0.5%. This latter figure is approximately constant for different sulfite samples and does not appear to depend on the method by which the process is carried out.

The following table shows the amount of resin obtained by W. Herzberg, from various types of purified wood pulp.

TABLE XXXI.—RESINS IN WOOD PULP.

	Per cent.
Mitscherlich cellulose, unbleached....	0.58
Mitscherlich cellulose, bleached......	0.44
Ritter Kellner cellulose, unbleached....	0.59
Ritter Kellner cellulose, bleached.....	0.45
Sulfite process, unbleached...........	0.72
Sulfite process, bleached.............	0.43
Sodium sulfite, unbleached...........	0.04
Sodium sulfite, bleached.............	0.03

The resin in the above celluloses is separated, for estimation, by extraction with ether.

The differences in the physical condition of wood pulp obtained in various methods and from different types of wood may produce nitrocelluloses with widely varying physical properties. To secure uniform products from different woods A. Luck and E. Durnford[1] destroy the physical structure of the wood before nitration. This is brought about by first treating the cellulose material with known solvents so as to effect solution. Such solvents as aqueous sulfuric acid, zinc chloride in hydrochloric acid or caustic soda, carbon bisulfide and water are advocated. The cellulose is separated in a hydrated form in the usual way after freeing from traces of solvent. A compact powdery material is then obtained which, on nitration and purification, is said to give a dense, granular nitrocellulose.

P. Girard[2] purifies wood pulp by subjecting it to the action

---

[1] 1. E. P. 4769, 1895; abst. J. S. C. I. 1896, **15**, 135. H. Opl, D. R. P. 75351, 1893; Ber. 1894, **27**, 836. Reid, Dingl. Poly. 1886, **261**, 379; J. S. C. I. 1886, **5**, 273; Wag. Jahr. 1886, 984. A. Sparre, D. R. P. 237081, 1911; abst. Zts. Chem. Ind. Koll. 1912, **10**, 111; Wag. Jahr. 1911, **57**, II, 500; Chem. Zentr. 1911, **82**, II, 411; Chem. Ztg. Rep. 1911, **35**, 481; Ztg. ang. Chem. 1911, **24**, 1583.

[2] 2. F. P. 443897; abst. Kunst. 1913, **3**, 15. Many of the essential ideas of this process are to be found in E. P. 1454, 1860, L. Obert, J. Vasseur and A. Houbigant. E. Steiger and E. Schulze, Ber. 1890, **23**, 3110; abst. J. C. S. 1891, **60**, 33; Jahr. Chem. 1890, **36**, 2188. B. Tollens and W. Stone, Ber. 1888, **21**, 1572; abst. J. C. S. 1888, **54**, 808; J. S. C. I. 1888, **7**, 511.

of solvents which do not attack the cellulose, but which dissolve the other products. It is claimed that the resulting product is equal to the more expensive forms of cellulose obtained from cotton and other sources. The extracted materials such as resin, etc., can be regained from the solvent by evaporation. The solvents used are methyl, ethyl, or amyl alcohols, acetone, carbon tetrachloride, chlorine derivatives of ethane or ethylene, as for example, trichloroethylene, either singly or in combination, or when mixed with 5%–10% of formaldehyde solution. The use of formaldehyde has two purposes: it acts as an antiseptic and causes a matting together of the substance that is being extracted. The water appears to preserve the porosity of the mass so that the solvent penetrates into the structure of the wood.

V. Drewsen has described a process of refining sulfite[1] or sulfate[2] wood pulp for nitrating purposes, the invention relating especially to the refining or purification of wood pulp produced from pine, spruce, or similar suitable wood, by either the caustic soda or sulfate process or sulfite or acid process, to secure a refined pulp of low caustic potash solubility with minimum loss of the original wood pulp material.

In carrying this process into effect the original wood pulp is preferably partially bleached with chlorine water so as to considerably change some of the colored compounds, thus giving the wood pulp a grayish yellow or yellowish tinge, the colored material being removed by a cooking process with sodium carbonate or sodium hydroxide.

The pulp, after this treatment, has a considerably reduced caustic potash solubility and is said to be sufficiently light in color to be used without serious objection for some nitrating processes. If desired, however, the treated pulp may be given a second bleaching action with a relatively small proportion of bleaching powder solution to still further improve its color without

---

[1] U. S. P. 1283114, 1918. C. Rosenhain, Deutsche Industrieztg. 1875, 502; Chem. Centr. 1877, **48**, 103; Dingl. Poly. 1876, **220**, 81. H. Spindler, Chem. Ztg. 1897, **21**, 302.

[2] U. S. P. 1283113, 1918. A. Ullmann, Aus. P. 3043, 1890. E. Unger and R. Jaeger, Ber. 1903, **36**, 1222; abst. Chem. Centr. 1903, I, 1194; J. C. S. 1903, **84**, ii, 456. B. Wagner, D. R. P. 188428, 1906; abst. Pap. Ztg. 1907, **32**, 3356; Wochenbl. Papierfab. 1907, **38**, 3519; Wag. Jahr. 1907, **53**, I, 10; Chem. Ztg. Rep. 1907, **31**, 491.

undesirably increasing its percentage of caustic potash solubility.

Wood pulp[1] contains about the same (91%–92%) quantity of cellulose. Mitscherlich and Ritter-Kellner sulfite pulps contain the smallest amount of pentosans and soda pulp the most. There, however, is not much difference in the lignin content of the pulp. Sulfite pulps yield about 0.7% ether-extract and soda pulps about 0.2%.

The development of this art from a practical point of view, is clearly set out in the work of A. Frank,[2] M. Elb,[3] C. Eckman,[4] L. Dorenfeldt,[5] F. Ahrens,[6] T. Knoesel,[7] A. Kumpfmiller,[8] M.

---

1. C. Schwalbe, Zts. ang. Chem. 1918, **31**, 50; abst. J. S. C. I. 1918, **37**, 365-A; C. A. 1918, **12**, 2439. C. Weilberg, U. S. P. 981042; J. S. C. I. 1911, **30**, 204. F. Wendenberg, D. R. P. 32329; Pap. Ztg. 1886, **11**, 188.

2. D. R. P. 40308, 1886; abst. Wag. Jahr. 1887, **33**, 1177. Aust. P. 646, 1887; Ber. 1887, **20**, 667; Dingl. Poly. 1888, **268**, 485; **276**, 58; Zts. Papierzeugung Verbrauch, 1888, **2**, 733; Wochenbl. Papierfabr. 1904, **35**, 3338; Pap. Ztg. 1886, **11**, 541, 1387; 1887, **12**, 137, 1170, 1765, 1782, 1823; 1889, **14**, 123, 383, 1091, 1488, 1556; 1890, **15**, 1398; 1891, **16**, 1813; 1892, **17**, 791; 1904, **29**, 2465, 3368. See D. Frank, E. P. 5532, 1882; abst. J. S. C. I. 1882, **1**, 244. Forbes, U. S. P. 510168; Dingl. Poly. 1896, **300**, 50.

3. D. R. P. 166947, 1905; abst. Wag. Jahr. 1906, **52**, II, 547; Jahr. Chem. 1905–1908, II, 973. Aust. P. 23146, 1905; abst. Chem. Centr. 1906, **77**, I, 801; Pap. Ztg. 1906, **31**, 152. D. R. P. 173686, 1905; abst. Pap. Ztg. 1906, **31**, 3180; Chem. Centr. 1906, **77**, II, 924. X. Zawadski and E. Meyer, D. R. P. 45951, 1888; Ber. 1889, **22**, 75; Pap. Ztg. 1889, **14**, 388.

4. E. P. 20036, 1893. D. R. P. 81643, 1893. Aust. P. 569, 1894; 3229, 1899; Ber. 1896, **28**, 711; Pap. Ztg. 1895, **20**, 2524; Chem. Ztg. 1895, **19**, 605; Pap. Ztg. 1896, **21**, 2218, 2609, 3247. Wochenbl. f. Papierfab. 1904, **35**, 461; abst. J. S. C. I. 1904, **23**, 265. G. Eichelbaum, D. R. P. 96316, 1897; Pap. Ztg. 1898, **23**, 1404; abst. Chem. Centr. 1898, **69**, I, 1288. Erste Oesterreichische Sodafabrik, Aust. P. 2336, 1899.

5. D. R. P. 113435; abst. Wag. Jahr. 1900, **46**, II, 530; Chem. Centr. 1900, 71, II, 702; Chem. Ztg. 1900, **24**, 762; Jahr. Chem. 1900, **53**, 848; 1901, 54, 899; 106021; 1898; abst. Wag. Jahr. 1899, **45**, 1063; Chem. Centr. 1900, **71**, 636; Zts. ang. Chem. 1899, **12**, 1161; Jahr. Chem. 1900, **53**, 848; 122489, 1898; abst. Wag. Jahr. 1901, **47**, II, 591; Chem. Centr. 1901, **72**, II, 248; Chem. Ztg. 1901, **25**, 631; Zts. ang. Chem. 1901, **14**, 808; 129227, 1900. Aust. P. 3807, 4602, 5062, 1898; abst. Pap. Ztg. 1900, **25**, 384, 2916; Wag. Jahr. 1902, **48**, II, 569; Chem. Centr. 1902, **73**, I, 686; Chem. Ztg. 1902, **26**, 233; Papier Ztg. 1903, **28**, (7), 215; abst. J. S. C. I. 1903, **22**, 160. A. Denison and H. Palmer, U. S. P. 496000. D. R. P. 73924; Dingl. Poly. 1894, **292**, 123; Wag. Jahr. 1894, **40**, 1059.

6. Zts. ang. Chem. 1895, **8**, 41; Chem. Centr. 1895, **66**, I, 569; Ber. 1895, **28**, 238; Pap. Ztg. 1895, **20**, 562; 1905, **30**, 1539; Chem. Zts. 1905, **4**, 40. L. Abraham, Aust. Anm. A-5635, 1909; D. R. P. 224411; Pap. Ztg. 1910, **35**, 2140; Wochenbl. Papierfabr. 1910, **41**, 1111, 2613; Wag. Jahr. 1910, **56**, II, 454; Chem. Zentr. 1910, **81**, II, 614. Dresel, D. R. P. 5891. Duerr & Co., D. R. P. 71942, 1893; abst. Ber. 1894, **27**, 220; Pap. Ztg. 1894, **19**, 76; Wag. Jahr. 1894, **40**, 1060; Jahr. Chem. 1894, **47**, 1135. B. Diamond, U. S. P. 938128, 1909; D. R. P. 216798, 1907; abst. Chem. Ztg. Rep. 1909, **33**, 607, 624; Wag. Jahr. 1909, **55**, I, 492; Chem. Zentr. 1910, **81**, I, 213; Chem. Ztg. Rep. 1909, **33**, 670; Zts. ang. Chem. 1910, **23**, 227; Jahr. Chem. 1910, **63**,

Hoenig,[1] B. Philippi,[2] J. Robeson,[3] J. Schwager,[4] D. Stewart,[5]

I, 362.

7. Chem. Ztg. 1902, **26,** 229; Chem. Centr. 1902, **73,** I, 955; Pap. Ztg. 1903, **28,** 288; Wochenbl. Papierf. 1907, **38,** 1293, 2542; 1908, **39,** 3276; 1908, **40,** 4049; 1909, **40,** 1603; abst. J. S. C. I. 1909, **28,** 671. F. Zenk, Pap. Ztg. 1894, **19,** 688, 699, 733, 796, 893, 928, 961. A. Zimmermann, Pap. Ztg. 1897, **22,** 947.

8. D. R. P. 81338, 1894; Ber. 1896, **28,** 686; Chem. Centr. 1895, **66,** II, 472; Pap. Ztg. 1895, **20,** 2030, 2072. Chem. Ztg. 1910, **34,** 19; abst. J. S. C. I. 1911, **30,** 19. See also D. R. P. 194127; abst. Wag. Jahr. 1908, **54,** I, 506; Chem. Zentr. 1908, **79,** I, 1124; Chem. Ztg. Rep. 1908, **32,** 139. D. R. P. 194744; abst. Wag. Jahr. 1908, **54,** I, 506; Chem. Ztg. Rep. 1908, **32,** 145. D. R. P. 194745; abst. Wag. Jahr. 1908, **54,** I, 506; Chem. Zentr. 1908, **79,** I, 1124; Chem. Ztg. Rep. 1908, **32,** 135. D. R. P. 196390; abst. Wag. Jahr. 1908, **54,** I, 506; Chem. Zentr. 1908, **79,** I, 1352; Chem. Ztg. Rep. 1908, **32,** 239. D. R. P. 197160. D. R. P. 197587; abst. Wag. Jahr. 1909, **55,** II, 287; Chem. Zentr. 1908, **79,** I, 1819; Chem. Ztg. Rep. 1908, **32,** 287. D. R. P. 201052, abst. Wag. Jahr. 1908, **54,** I, 506; Chem. Ztg. Rep. 1908, **32,** 632. D. R. P. 202393, 204470. D. R. P. 206743, abst. Wag. Jahr. 1909, **55,** I, 514; Chem. Ztg. Rep. 1909, **33,** 107. D. R. P. 206743, abst. Wag. Jahr. 1909, **55,** I, 514; Chem. Ztg. Rep. 1909, **33,** 107. D. R. P. 206999, abst. Wag. Jahr. 1909, **55,** I, 514. D. R. P. 207355, 208373. D. R. P. 83438, 1894; Ber. 1896, **28,** 1030; Pap. Ztg. 1896, **21,** 236; Wag. Jahr. 1895, **41,** 746; Zts. ang. Chem. 1896, **9,** 25; Jahr. Chem. 1895, **48,** 1356. D. R. P. 183415, 1905; Aust. P. 5849, 1894; Chem. Zentr. 1907, **78,** II, 109; Wochenbl. Papierfabr. 1907, **38,** 1402; Pap. Ztg. 1907, **32,** 2046; Chem. Ztg. Rep. 1907, **31,** 243. D. R. P. 189177, 1904; abst. Wag. Jahr. 1907, **53,** I, 8; Chem. Ztg. Rep. 1907, **31,** 491; 176722; abst. Chem. Ztg. Rep. 1907, **31,** 109; 195286; abst. Wag. Jahr. 1908, **79,** I, 5; Chem. Ztg. Rep. 1908, **32,** 176; 199279, abst. Chem. Zentr. 1908, **79,** I, 1118; Pap. Ztg. 1907, **32,** 3356; Wochenbl. Papierfabr. 1907, **38,** 3019. D. R. P. 194872, 1906; 183415; Chem. Zentr. 1908, **79,** I, 1118; Pap. Ztg. 1908, **33,** 896; Chem. Ztg. Rep. 1908, **32,** 255; Wochenbl. Papierfab. 1908, **39,** 1306. D. R. P. 207776, 1906; Papierfabr. 1909, **7,** 293; Pap. Ztg. 1909, **34,** 986; Chem. Ztg. Rep. 1909, **33,** 195. D. R. P. 216284, 1907; abst. Chem. Ztg. Rep. 1909, **33,** 627, 631; Pap. Ztg. 1909, **34,** 3716; Wag. Jahr. 1909, **55,** II, 507; Chem. Zentr. 1909, **80,** II, 2108; Chem. Ztg. 1909, **33,** 631. D. R. P. 203648, 1906; Aust. P. 40657, 1906; Chem. Zentr. 1908, **79,** II, 1834; Pap. Ztg. 1908, **33,** 3564; Chem. Ztg. 1908, **32,** 1036; Wochenbl. Papierfabr. 1909, **40,** 260. U. S. P. 940394, 1909; Chem. Ztg. Rep. 1909, **33,** 648; Pap. Ztg. 1910, **35,** 300. T. Korndorff, D. R. P. 32696, abst. Wag. Jahr. 1885, **31,** 1192; Pap. Ztg. 1886, **11,** 259. Knoeselmehl, D. R. P. 128213; Chem. Ztg. 1902, **26,** 229; 1903, **27,** 21; 1904, **28,** 38; Chem. Centr. 1902, **73,** I, 955; Pap. Ztg. 1903, **28,** 288; 1905, **30,** 1539; 1904, **29,** 3367; Chem. Zts. 1905, **4,** 40; Zts. ang. Chem. 1904, **17,** 1788. D. Kempe, Aust. P. 3962, 1897. G. Katz, D. R. P. 149461, 1903; abst. Wag. Jahr. 1904, **50,** II, 533; Pap. Ztg. 1904, **29,** 800; Chem. Ztg. 1904, **28,** 217; Zts. ang. Chem. 1904, **17,** 535; Jahr. Chem. 1904, **57,** 1164. O. Karr, U. S. P. 762139; Pap. Ztg. 1904, **29,** 2726.

1. D. R. P. 132224, 1901; abst. Wag. Jahr. 1902, **48,** II, 600; Chem. Centr. 1902, **73,** II, 174; Chem. Ztg. 1902, **26,** 611. 152236; abst. Wag. Jahr. 1904, **50,** II, 514; Chem. Ztg. 1904, **28,** 648; Zts. ang. Chem. 1904, **17,** 1256. Aust. P. 7325, 1901; 12970, 1902; 31862, 1906; Pap. Ztg. 1902, **27,** 2162. J. Hough, U. S. P. 931608, 945394, 1910; J. S. C. I. 1909, **28,** 1148; Pap. Ztg. 1904, **34,** 2787. J. Hanson, E. P. 12261, 1885; abst. J. S. C. I. 1886, **5,** 614; Pap. Ztg. 1887, **12,** 352. E. Haenisch and M. Schroder, D. R. P. 36721, 1886; abst. Dingl. Poly. 1886, **262,** 418; Wag. Jahr. 1886, **32,** 267;

E. Trainer,[1] J. Vogel[2] and other investigators in this field.

Chem. Centr. 1887, **58,** 159; Bied. Tech. Chem. Jahr. 1886-87, **9,** 109.

2. D. R. P. 195643, 1904; abst. Chem. Zentr. 1908, **79,** I, 1232; Pap. Ztg. 1908, **33,** 1210; Wag. Jahr. 1908, **54,** II, 557; Chem. Ztg. Rep. 1908, **32,** 169. D. R. P. 211348, 1905; abst. Pap. Ztg. 1909, **34,** 2294; Wag. Jahr. 1909, **55,** II, 563; Chem. Zentr. 1909, **80,** II, 400; Chem. Ztg. Rep. 1909, **33,** 447. G. Pictet, D. R. P. 26331, 1883; 41703, 1887; abst. Wag. Jahr. 1884, **30,** 1147; 1888, **34,** 398; Pap. Ztg. 1884, **9,** 562. E. Pollacsek, Aust. P. 967, 985, 1524, 1898. Pissier, E. P. 12762, 1887. A. Selkirk, E. P. 11848, 1888; abst. J. S. C. I. 1888, **7,** 864.

3. E. P. 17956, 1908. Aust. P. 42479, 1909. U. S. P. 851378, 851381; J. S. C. I. 1909, **28,** 1052; Chem. Ztg. 1907, **31,** 312; Pap. Ztg. 1910, **35,** 300. E. Rinman, D. R. P. 222302, 1909; abst. Pap. Ztg. 1910, **35,** 1726; Wochenbl. Papierfab. 1910, **41,** 1869; Papierfabr. 1910, **8,** 536; Wag. Jahr. 1910, **56,** II, 453; Chem. Zentr. 1910, **81,** II, 52; Chem. Ztg. Rep. 1910, **34,** 299; Zts. ang. Chem. 1910, **23,** 1390. P. Remy, D. R. P. 90798, 1896; abst. Pap. Ztg. 1897, **22,** 426; Wag. Jahr. 1897, **43,** 10; Chem. Ztg. 1897, **21,** 229.

4. D. R. P. 53043, 1889; 58599, 1890; 87678, 1895; 96434, 1897; 115256, 1900; 128903, 1901; 148331; abst. Wag. Jahr. 1890, **36,** 600; 1891, **37,** 868; 1896, **42,** 790; 1901, **47,** II, 311; 1902, **48,** I, 519; Chem. Ztg. 1896, **20,** 726; 1902, **26,** 410; Jahr. Chem. 1898, **51,** 172; Chem. Centr. 1898, **69,** II, 458; Zts. ang. Chem. 1901, **14,** 94; 1902, **15,** 314; Ber. 1890, **23,** 159; Pap. Ztg. 1903, **28,** 2075, 2183.

5. U. S. P. 909343, 1909. Aust. P. 40528, 1907; Chem. Ztg. Rep. 1909, **33,** 175. U. S. P. 923088, 1909; abst. J. S. C. I. 1908, **28,** 737. J. Stanley, U. S. P. 968278. E. P. 29087, 1910; abst. J. S. C. I. 1911, **30,** 951. D. Sparre, D. R. P. 237081; abst. Wag. Jahr. 1911, **57,** 500; Chem. Zentr. 1911, **82,** II, 411; Chem. Ztg. Rep. 1911, **35,** 481; Zts. ang. Chem. 1911, **24,** 1583. A. Schweinberg, Aust. P. 14423, 1902. W. Schacht, D. R. P. 122171, 131108; abst. Wag. Jahr. 1901, **47,** II, 590; 1902, **48,** II, 566; Chem. Ztg. 1901, **25,** 707; 1902, **26,** 462. Papier Ztg. 1901, **26,** (84), 3143; abst. J. S. C. I. 1901, **20,** 1230.

1. D. R. P. 136322, 1900; 140542, 140862, 144819, 1902; 161675, 1903; 181126, 1905; 197195, 202132, 1906. Aust. P. 36847; Pap. Ztg. 1902, **27,** 3478; 1903, **28,** 86, 1332, 1942, 3086, 3478; 1905, **30,** 2582; 1907, **32,** 994; 1908, **33,** 3238; Wochenbl. Papierfabr. 1907, **38,** 1307; 1908, **39,** 2539, 3466; Zts. ang. Chem. 1908, **21,** 1194; Chem. Zentr. 1908, **79,** I, 1595; II, 1389; 1907, **78,** II, 109; Pap. Fabrik. 1907, 641. E. Trippe, D. R. P. 133312, 1901; abst. Wag. Jahr. 1902, **48,** II, 568; Chem. Centr. 1902, **73,** II, 410; Chem. Ztg. 1902, **26,** 737; Zts. ang. Chem. 1902, **15,** 765.

2. D. R. P. 215273; Pap. Ztg. 1906, **31,** 1278, 1314, 1355; 1907, **32,** 961, 1010, 1054, 1098; 1908, **33,** 3855, 3890, 3931; 1909, **34,** 3; Wochenbl. Papierfabr. 1907, **38,** 881, 958; 1909, **40,** 857, 930, 1110; Chem. Centr. 1906, **77,** I, 1853; Zts. ang. Chem. 1910, **23,** 116; Chem. Ztg. 1909, **33,** 1187. C. Voight, D. R. P. 33235, 40693, 1886; abst. Wag. Jahr. 1888, **34,** 1091. Verein f. Chemische Industrie, D. R. P. 25485, 31747; abst. Wag. Jahr. 1884, **30,** 1151; 1885, **31,** 1038.

For early history of utilization of pulp, see E. P. 2481, 1801, Koop. E. P. 5041, 1824, Lambert. E. P. 13979, 1852, Coupier and Mellier. E. P. 2219, 1853, Poole. E. P. 1942, 1853, U. S. P. 6854, 1854, Watt and Burgess. E. P. 2172, 1854, Mellier. E. P. 2488, 1854, Cashellain. E. P. 135, 1855, Johnson. E. P. 836, 1855, Cowley and Sullivan. E. P. 2019, 2315, 1855, Fraser. U. S. P. 12361. E. P. 4671, 1857, Houghton. U. S. P. 16202, Palser and Howland. E. P. 1997, 1859, Collyer. E. P. 1507, 1861, Watt. E. P. 1822, 1861, Henry. E. P. 2351, 1861, Grantham. E. P. 408, 467, 1863, Clark. E. P. 112, 1866, Stevens. E. P. 167, 1868, Fyfe. E. P. 1050, 1868, Baumann. E. P. 2793, 1868. E. P. 3392, 1870, Walsh. E. P. 748,

Wood Pulp for Esterification. In the conflict which has so

1870. E. P. 3139, 1870, Ruck. E. P. 3148, 1870, Wrigley. E. P. 1871, 1871, Richardson. E. P. 279, 1871, Annandale. E. P. 1422, 1871, Newton. U. S. P. 119224, Eaton. E. P. 257, 1872; D. R. P. 933, Ungerer. E. P. 1851, 1872, v. Baerle. E. P. 2147, 1872, Blyth and Southly. E. P. 695, 863, 1873, Lee. E. P. 2956, 1874, Tiffany.

See also: A. Aberg, U. S. P. 691091, 1902; abst. J. S. C. I. 1902, **21**, 272. J. Abom, E. P. 8964, 1894; abst. J. S. C. I. 1894, **13**, 824. Aflenzer-Graphit-und Talksteingewerkschaft, D. R. P. 277385, 1913; abst. J. S. C. I. 1915, **34**, 173. E. Ahlfors and H. Helin, Papier-Fabrikant, 1909, **7**, 287–289; abst. J. S. C. I. 1909, **28**, 438. A. Ahlin, Papier Ztg. 1902, **27**, (33), 1178; 1908, **33**, 1181–1182; J. S. C. I. 1902, **21**, 134; abst. J. S. C. I. 1902, **21**, 718; 1908, **27**, 517. Akt.-Ges. f. Zellstoff-und Papierfabr. D. R. P. 309551, 1916; J. S. C. I. 1919, **38**, 218-A. J. Aktschourin, E. P. 18191, 1911; abst. J. S. C. I. 1912, **31**, 871; see F. P. 433424, 1911; abst. J. S. C. I. 1912, **31**, 225; U. S. P. 1169592, 1915; abst. J. S. C. I. 1916, **35**, 303. E. Allen and B. Tollens, Ann. 1890, **260**, 289–306; abst. J. S. C. I. 1891, **10**, 473. S. Allen, U. S. P. 253656, 1882; abst. J. S. C. I. 1882, **1**, 116. J. Almond and S. Andrews, E. P. 24600 1898; abst. J. S. C. I. 190, **19**, 67. E. Altmann, Chem.-Ztg. 1911, **35**, 979; abst. J. S. C. I. 1911, **30**, 1154. P. Ammon, Paper-making, 1909, **28**, 437; abst. J. S. C. I. 1909, **28**, 1269. J. Annandale, F. P. 345044, 1904; abst. J. S. C. I. 1904, **23**, 1159; see E. P. 26012, 1903; abst. J. S. C. I. 1904, **23**, 1040; E. P. 14558, 1889; abst. J. S. C. I. 1891, **10**, 62. E. Applegarth, E. P. 2832, 1890; abst. J. S. C. I. 1891, **10**, 268. C. D. Aria, E. P. 8981, 1888; abst. J. S. C. I. 1889, **8**, 565. G. Archbold, Ber. 1883, **16**, 350; abst. J. S. C. I. 1883, **2**, 295. H. Arledter, F. P. 418584, 1910; abst. J. S. C. I. 1911, **30**, 80. E. P. 20395, 1911; abst. J. S. C. I. 1912, **31**, 981. U. S. P. 1153883, 1915; abst. J. S. C. I. 1915, **34**, 1087; U. S. P. 1048123, 1912; abst. J. S. C. I. 1913, **32**, 81. E. P. 2018, 1910; abst. J. S. C. I. 1911, **30**, 205. L. Atwood, U. S. P. 698428, 1902; abst. J. S. C. I. 1902, **21**, 788. A. Audibert, F. P. 403151, 1909; abst. J. S. C. I. 1909, **28**, 1323. C. Bache-Wüg, E. P. 944, 1914; abst. J. S. C. I. 1914, **33**, 417. U. S. P. 1084244, 1914; abst. J. S. C. I. 1914, **33**, 196. U. S. P. 1240920, 1917; abst. J. S. C. I. 1917, **36**, 1174. U. S. P. 903679, 1909; abst. J. S. C. I. 1909, **28**, 381. C. Badoil, F. P. 382439, 1907; abst. J. S. C. I. 1908, **27**, 244; F. P. 392750, 1908; abst. J. S. C. I. 1909, **28**, 38. A. Badoil and J. Valadon, F. P. 338477, 1903; abst. J. C. S. I. 1904, **23**, 677. L. Baekeland, U. S. P. 1160362, 1915; abst. J. S. C. I. 1915, **34**, 1244. U. S. P. 1160365, 1915; abst. J. S. C. I. 1915, **34**, 1245. A. Baker and J. Jennison, Paper and Pulp, Jan. 1910; Sindall and Heckford, Paper Trade Review, Oct. 7, 1904; abst. J. S. C. I. 1914, **33**, 284. J. Barker, G. Sheolin and F. Barker, U. S. P. 693215, 1902; abst. J. S. C. I. 1902, **21**, 362. A. Barthelemy, F. P. 369657, 1906; abst. J. S. C. I. 1907, **26**, 220. C. Bartsch, Papierfabrikant, 1911, **9**, 23; J. S. C. I. 1911, **30**, 414, 887. J. Bates, abst. J. S. C. I. 1918, **37**, 457-R. J. Baudisch, Papier Ztg. 1891, **16**, 2414–2415; J. S. C. I. 1888, **7**, 863; 1889, **8**, 574, 1891, **10**, 576; 1892, **11**, 464. F. Baumann, D. R. P. 22177, 1882; abst. J. S. C. I. 1883, **2**, 359. F. Bayer & Co., E. P. 10729, 1907; abst. J. S. C. I. 1908, **27**, 138. D. R. P. 283107, 1913; abst. J. S. C. I. 1915, **34**, 729. F. P. 385944, 1908; abst. J. S. C. I. 1908, **27**, 707. C. Beadle, U. S. P. 1286502, 1918; abst. J. S. C. I. 1919, **38**, 131-A; E. P. 116005, 1917; abst. J. S. C. I. 1918, **37**, 409-A. Paper and Pulp, 1905, **10**, 297–301; abst. J. S. C. I. 1905, **24**, 633. C. Beadle and H. Stevens, Chem. News, 1907, **95**, 193; abst. J. S. C. I. 1907, **26**, 548; Chem. News, 1914, **109**, 302–304; abst. J. S. C. I. 1914, **33**, 745; Paper-making, 1914, **47**, 397–403; J. S. C. I. 1913, **32**, 1103; abst. J. S. C. I. 1914, **33**, 545; Papermaker, 1913, **45**, 150–157; abst. J. S. C. I. 1913, **32**, 1103; Eighth Int. Cong. Appl. Chem. 1912, **13**, 25; 1912, Sect. VI^{a} Orig., Comm. **13**, 265; abst. J. S. C. I. 1913, **32**, 174. Eighth Int. Cong. Appl. Chem. 1912, Sect.

recently closed, while by far the major portion of the cellulose

---

VI^{a} Orig. Comm. **13,** 39–45; abst. J. S. C. I. 1912, **31,** 870; abst. J. S. C. I. 1909, **28,** 1015; J. S. C. I. 1913, **32,** 217. W. Beaumont, E. P. 24904, 1898; abst. J. S. C. I. 1899, **18,** 392. E. Belani, Der Papierfabrikant, 1908, **6,** 604–605; abst. J. S. C. I. 1908, **27,** 707. J. Bell, abst. J. S. C. I. 1894, **13,** 117. J. Beltzer, Bull. Soc. Chim. 1910, **7,** 294–300, 361–367; abst. J. S. C. I. 1910, **29,** 690. J. Bennett and W. Appleyard, E. P. 9716, 1899; abst. J. S. C. I. 1899, **18,** 782. W. Benso and B. Jirotka, E. P. 26824, 1911; abst. J. S. C. I. 1913, **32,** 421. A. Berge, Bull. Soc. Chim. Belg. 1906, **20,** 158–159; abst. J. S. C. I. 1906, **25,** 912. E. Bergerhoff, D. R. P. 279411, 1914; abst. J. S. C. I. 1915, **34,** 419; D. R. P. 160651, 1903; 163070, 1904; abst. J. S. C. I. 1905, **24,** 1028; 1906, **25,** 37. A. Berget, U. S. P. 683836; Papier Ztg. 1901, **26,** (92), 3427; abst. J. S. C. I. 1902, **21,** 64. F. Berguis and E. Hägglund, D. R. P. 311933, 1917; abst. J. S. C. I. 1917, **36,** 760-A. A. Bergöö, Papierfabrikant, 1912, **10,** 419–422; abst. J. S. C. I. 1912, **31,** 427. D. Bertram and S. Milne, E. P. 8275, 1899; abst. J. S. C. I. 1900, **19,** 552. G. Bertrand, Compt. rend. 1898, **127,** (2), 124–127; 1899, **126,** 762, 842 and 984; Bull. Soc. Chim. 1898, **15,** 592; abst. J. S. C. I. 1898, **17,** 936. P. Billon, F. P. 363279, 1906; abst. J. S. C. I. 1906, **25,** 865. H. Bird, E. P. 16375, 1892; abst. J. S. C. I. 1893, **12,** 461. R. Birkholz, U. S. P. 787971, 1905; abst. J. S. C. I. 1905, **24,** 558. A. Bloxam, E. P. 116604, 1917 (Appl. No. 11536, 1917); abst. J. S. C. I. 1918, **37,** 461-A. A. Boake and G. Roberts, E. P. 8840, 1888; abst. J. S. C. I. 1889, **8,** 565. L. Bohm, E. P. 14035, 1900; abst. J. S. C. I. 1900, **19,** 1034. U. S. P. 875315, 1907; abst. 1908, **27,** 178. J. Bonar, E. P. 8214, 1911; abst. J. S. C. I. 1912, **31,** 428. E. Bosaeus, Kemi-och Bergvetenskap, 1910, Part 3; Papierfabrikant, 1910, **8,** 737–739, 767–770; J. S. C. I. 1910, **29,** 343; abst. J. S. C. I. 1910, **29,** 1052. G. Boulais and P. Lefevre, F. P. 465534, 1913; abst. J. S. C. I. 1914, **33,** 608. D. Bowack, R. Heald and A. Davis, Aynsome Annual, 1911, **3,** 62–75; World's Paper Trade Rev. 1911; abst. J. S. C. I. 1912, **31,** 582. P. Boy, F. P. 350117, 1904; abst. J. S. C. I. 1905, **24,** 1169. C. Brand, U. S. Dep't Agric. Bureau of Plant Industry, Circular No. 82, August 31, 1–19; abst. J. S. C. I. 1912, **31,** 120. C. Brand and J. Merrill, U. S. Dep't Agric. Bull. No. 309, Nov. 4, 1915, 1-27; abst. J. S. C. I. 1916, **35,** 417. C. Braun, D. R. P. 261848, 1912; abst. J. S. C. I. 1913, **32,** 823; D. R. P. 279517, 1913; abst. J. S. C. I. 1915, **34,** 419. J. Briggs, World's Paper Trade Rev. 1911; Papierfabrikant, 1911, **9,** 1340–1341; abst. J. S. C. I. 1911, **30,** 1374. A. Brin, E. P. 15720, 1892; abst. J. S. C. I. 1893, **12,** 858. A. and L. Brin, E. P. 4953, 1887; abst. J. S. C. I. 1888, **7,** 33. H. Bristol, Papierfabr. 1911, **9,** 309–312; abst. J. S. C. I. 1911, **30,** 413. C. Brodbeck, E. P. 23598, 1895; abst. J. S. C. I. 1897, **16,** 327. O. Brune, D. R. P. 310554, 1917; abst. J. S. C. I. 1919, **38,** 357-A. C. Bullard, Eighth Int. Cong. Appl. Chem. 1912, Sect. VI^{a}. Orig. Comm. **13,** 77–82; abst. J. S. C. I. 1912, **31,** 869. J. Burby, F. P. 444703, 1912; abst. J. S. C. I. 1912, **31,** 1075; U. S. P. 1029848, 1912; abst. J. S. C. I. 1912, **31,** 680. T. Burgess, U. S. P. 693684, 1902; abst. J. S. C. I. 1902, **21,** 494. W. Burton, D. R. P. 226912, 1909; abst. J. S. C. I. 1911, **30,** 80. F. Bushbridge, U. S. P. 789792, 1905; abst. J. S. C. I. 1905, **24,** 633. E. P. 25075, 1903; abst. J. S. C. I. 1904, **23,** 677. F. P. 342265, 1904; abst. J. S. C. I. 1904, **23,** 949. W. Caldwell, E. P. 15332, 1893; abst. J. S. C. I. 1894, **13,** 1085. W. Callender, E. P. 20346, 1900; abst. J. S. C. I. 1901, **20,** 831. T. Carlson, Kemi och Bergsvetenskap, 1910, (1); Wochenbl. Papierfabr. 1910, **41,** 551–552; abst. J. S. C. I. 1910, **29,** 343. J. and F. Carmichael, F. P. 329107, 1903; abst. J. S. C. I. 1903, **22,** 1012. O. Carr, U. S. P. 762139, 1904; 1089691, 1914; abst. J. S. C. I. 1904, **23,** 725; 1914, **33,** 417. H. Carriere, F. P. 329445, 1903; abst. J. S. C. I. 1903, **22,** 1062. B. Cataldi, E. P. 101475, 1916 (Appl. No. 12862 of 1916); abst. J. S. C. I. 1917, **36,** 1232. B. Cawthorn and J. Cornett, E. P. 2923, 1894; abst. J. S. C. I. 1895, **14,** nitrated and acetated in the Entente countries was some form of

183. J. De Cew, J. S. C. I. 1907, **26,** 561. W. Chaplin, F. P. 449943, 1912; abst. J. S. C. I. 1913, **32,** 482. L. Chaptal and J. Gaisset, F. P. 446382, 1912; abst. J. S. C. I. 1913, **32,** 133. F. Cheesbrough, E. P. 9694, 1889; abst. J. S. C. I. 1890, **9,** 321. C. Classen, E. P. 9579, 1908; abst. J. S. C. I. 1909, **28,** 363. A. Clark, E. P. 3240, 1883; abst. J. S. C. I. 1884, **3,** 190; E. P. 11557, 1884; abst. J. S. C. I. 1884, **3,** 645. F. Clark, School of Mines Quarterly, **9,** 162–177; abst. J. S. C. I. 1888, **7,** 497. G. Clark, U. S. P. 696314, 1902; abst. J. S. C. I. 1902, **21,** 635. M. Cline and J. Thickens, Eighth Int. Cong. Appl. Chem. 1912, Sect. VI^a, Orig. Comm. **13,** 83–99; abst. J. S. C. I. 1912, **31,** 869. M. Cram, J. Ind. Eng. Chem. 1914, **6,** 896; abst. Chem. Zentr. 1915, I, 860. T. Cobley, E. P. 3599, 1883; abst. J. S. C. I. 1884, **3,** 328. W. Cohoe, U. S. P. 985725 and 985726, 1911; abst. J. S. C. I. 1911, **30,** 441. E. P. 23573, 1910; abst. J. S. C. I. 1912, **31,** 86. J. Colby, D. R. P. 157763, 1902; abst. J. S. C. I. 1905, **24,** 633. J. Cornett, E. P. 14191, 1893; abst. J. S. C. I. 1893, **12,** 859. M. Coulon, Millheil, des k. k. Tech. Gew.-Museums, **2,** 28–34; abst. J. S. C. I. 1888, **7,** 843. P. Couper, E. P. 2774, 1905; abst. J. S. C. I. 1905, **24,** 1215. F. P. 361005, 1905; abst. J. S. C. I. 1906, **25,** 556. E. P. 9942 and 20355, 1913; abst. J. S. C. I. 1914, **33,** 478. G. Craighill and G. Kerr, U. S. P. 817960, 1906; abst. J. S. C. I. 1906, **25,** 494. W. Croll, U. S. P. 1165323, 1915, renewed May 20, 1915; abst. J. S. C. I. 1916, **35,** 250. E. P. 121318, 1918; abst. J. S. C. I. 1919, **38,** 31-A. W. Cross, Ber. 1910, **43,** 1526–1528; abst. J. S. C. I. 1910, **29,** 750. W. Curtis, E. P. 4945, 1898; abst. J. S. C. I. 1898, **17,** 789. A. Curtis and A. H. White, U. S. P. 1181967, 1916; abst. J. S. C. I. 1916, **35,** 686. G. Cushing, U. S. P. 788633, 1905; abst. J. S. C. I. 1905, **24,** 633. C. Dahl, U. S. P. 296935, 1884; E. P. 11150, 1888; abst. J. S. C. I. 1889, **8,** 814. A. Dassonville, F. P. 387104, 1908; abst. J. S. C. I. 1908, **27,** 817. First addition dated Sept. 3, 1908 to F. P. 387104, 1908 (J. S. C. I. 1908, **27,** 817); abst. J. S. C. I. 1909, **28,** 241. E. Davies and H. Goodfellow, E. P. 3288, 1896; abst. J. S. C. I. 1896, **15,** 554. W. Decker, U. S. P. 928247, 928248, 928249 of 1909; abst. J. S. C. I. 1909, **28,** 958. E. P. 26762, 1909; abst. J. S. C. I. 1910, **29,** 148. E. P. 15269, 1909; abst. J. S. C. I. 1910, **29,** 269. J. Desmarest, E. P. 26260, 1901; abst. J. S. C. I. 1903, **22,** 109. G. Devimeux, F. P. 409034, 1909; abst. J. S. C. I. 1910, **29,** 751. R. Dietz, Zts. ang. Chem. 1905, **18,** 647–653; abst. J. S. C. I. 1905, **24,** 557. W. Digby, Electrochem. and Metall. Ind. 1907, **5,** 178–182; abst. J. S. C. I. 1907, **26,** 712. J. Dohan, U. S. P. 865168, 1907; abst. J. S. C. I. 1907, **26,** 1107. H. and A. von Donnersmarck-Beutel, F. P. 353997, 1905; abst. J. S. C. I. 1905, **24,** 1081. C. Doree and M. Cunningham, Chem. Soc. Proc. 1913, **29,** 104–105; J. S. C. I. 1912, **31,** 278; abst. J. S. C. I. 1913, **32,** 482. B. Dorner, E. P. 8638, 1911; abst. J. S. C. I. 1911, **30,** 1376; U. S. P. 1038730, 1912; abst. J. S. C. I. 1912, **31,** 981. C. Doughty, U. S. P. 775525, 1904; abst. J. S. C. I. 1904, **23,** 1233. W. Dreaper, J. Soc. Dyers Col. 1912, **28,** 178–179; abst. J. S. C. I. 1912, **31,** 485. F. Dubrot, F. P. 396647, 1908; abst. J. S. C. I. 1909, **28,** 597. L. Dulfus, E. P. 3780, 1884; abst. J. S. C. I. 1885, **4,** 242. L. Echegut, F. P. 359550, 1905; abst. J. S. C. I. 1906, **25,** 388. Egoroff and A. Remmer, F. P. 410835, 1909; abst. J. S. C. I. 1910, **29,** 811. E. Eichhorn, F. P. 322177, 1902; abst. J. S. C. I. 1903, **22,** 315. R. Eichmann, D. R. P. 184991, 1906; abst. J. S. C. I. 1908, **27,** 244. G. Ekström, Papierfabrikant, 1910, **8,** 582; abst. J. S. C. I. 1910, **29,** 810. U. S. P. 1095830, 1914; abst. J. S. C. I. 1914, **33,** 659. C. Ellis, U. S. P. 1311595, 1919; abst. J. S. C. I. 1919, **38,** 678-A. R. Embree, U. S. P. 1203511, 1916; abst. J. S. C. I. 1916, **35,** 1257. C. Esser, U. S. P. 836069, 1906; abst. J. S. C. I. 1907, **26,** 112. E. P. 9589, 1901; abst. J. S. C. I. 1901, **20,** 830. L. Evans, E. P. 19808, 1905; abst. J. S. C. I. 1906, **25,** 950. H. Falk, Papierfabrikant, 1909, **7,** 469–474; J. S. C. I.

short fiber cotton immense quantities of wood pulp were esterified

1908, **27,** 1037; abst. J. S. C. I. 1909, **28,** 622. H. Falke, Färb. Ztg. 1894, **5,** 97–100, 113–116; abst. J. S. C. I. 1894, **13,** 399. Farnand, Wochenbl. Papierfab. 1909, **40,** 4449–4450; abst. J. S. C. I. 1910, **29,** 147. A. Faust, E. P. 21737, 1900; abst. J. S. C. I. 1901, **20,** 496. J. Feldschmid, abst. J. S. C. I. 1913, **32,** 975. J. Ferrand, U. S. P. 774982, 1904; abst. J. S. C. I. 1904, **23,** 1233. F. P. 327046, 1902; abst. J. S. C. I. 1903, **22,** 879. A. Fest, U. S. P. 1218638, 1917; abst. J. S. C. I. 1917, **36,** 451. A. von Festy, E. P. 7428, 1899; abst. J. S. C. I. 1899, **18,** 942. F. Finiels, F. P. 440329, 1911; abst. J. S. C. I. 1912, **31,** 812. F. Fischer and H. Niggemann, Ges. Abhand. zur. Kenntnis der Kohle, 1917, **1,** 176–183; Chem. Zentr. 1919, **90,** II, 521; abst. J. S. C. I. 1919, **38,** 494. E. Fleury, E. P. 11103, 1906; abst. J. S. C. I. 1907, **26,** 712. E. Foley, U. S. P. 1154851, 1915; abst. J. S. C. I. 1915, **34,** 1086. F. La Forge and C. S. Hudson, J. I. E. C. 1918, **10,** 925–927; abst. J. S. C. I. 1919, **38,** 86-A. J. Forshaw, E. P. 1292, 1914; abst. J. S. C. I. 1914, **33,** 1197. E. Fox, E. P. 20664, 1897; abst. J. S. C. I. 1898, **17,** 944. G. Frankforter, J. Ind. Eng. Chem. 1911, **3,** 4–10; abst. J. S. C. I. 1911, **30,** 1304. W. Freeman, F. P. 471620, 1913; abst. J. S. C. I. 1915, **34,** 419. E. P. 28929, 1913; abst. J. S. C. I. 1915, **34,** 488. Frohberg, Wochenbl. Papierfabr. 1911, **42,** 668–669; abst. J. S. C. I. 1911, **30,** 352; Wochenbl. Papierfabr. 1910, **41,** 1602–1606; abst. J. S. C. I. 1910, **29,** 688; Wochenbl. Papierfabr. 1910, **41,** 1179–1182; abst. J. S. C. I. 1910, **29,** 556; Wochenbl. Papierfabr. 1913, **44,** 3599–3601; abst. J. S. C. I. 1913, **32,** 974; Chem. Ztg. 1914, **38,** 126; abst. J. S. C. I. 1914, **33,** 857. K. Fromherz, Z. physiol. Chem. 1906, **50,** 209–240; Chem. Zentr. 1907, **1,** 643–645; J. S. C. I. 1905, **24,** 212; 1903, **22,** 114; abst. J. S. C. I. 1907, **26,** 339. A. Gagdeois, U. S. P. 848361, 1907; abst. J. S. C. I. 1907, **26,** 483. F. P. 360158, 1905; abst. J. S. C. I. 1906, **25,** 441. First addition 3823, to F. P. 306276, 1900; abst. J. S. C. I. 1905, **24,** 344. E. and W. Gelinek, E. P. 5178, 1893; abst. J. S. C. I. 1893, **12,** 858. G. Gemmell, abst. J. S. C. I. 1890, **9,** 165. D. Giaj-Tenua, F. P. 357374, 1905; abst. J. S. C. I. 1906, **25,** 88. R. Godeffroy, Mitt. k. k. techn. Gew. Museum, 1891, 295; 1888, 18, 62; 1889, 9; abst. J. S. C. I. 1892, **11,** 464. G. Goessmann, E. P. 10535, 1901; abst. J. S. C. I. 1902, **21,** 362. J. Goode, E. P. 18157, 1901; abst. J. S. C. I. 1903, **22,** 109. A. Gorz, E. P. 12096, 1898; abst. J. S. C. I. 1898, **17,** 944. L. Gottstein, Zts. ang. Chem. 1905, **18,** 983–984; abst. J. S. C. I. 1905, **24,** 748. O. Goy, E. P. 5339, 1903; abst. J. S. C. I. 1903, **22,** 817. A. Grandjean, E. P. 22566, 1894; abst. J. S. C. I. 1896, **15,** 132. E. Grandmougin, Ber. 1907, **40,** 2453; J. S. C. I. 1907, **26,** 633; J. S. C. I. 1906, **25,** 912; abst. J. S. C. I. 1907, **26,** 775. H. Green, U. S. P. 1206777, 1916. Renewed April 24, 1916; abst. J. S. C. I. 1917, **36,** 80. M. Griffin, Paper and Pulp, 1905, **10,** 492–496; abst. J. S. C. I. 1905, **24,** 937; J. S. C. I. 1890, **9,** 453. G. Gunn, E. P. 23947, 1908; abst. J. S. C. I. 1909, **28,** 541. B. Haas, Papierfabrikant, 1910, **8,** 74–78, 150–152, 177–178, 197–201; abst. J. S. C. I. 1910, **29,** 415. H. Haddan, E. P. 7495, 1885; abst. J. S. C. I. 1886, **5,** 435. H. Hadfield, Paper-Making, 1915, **34,** 206; abst. J. S. C. I. 1915, **34,** 830: B. Hafner and F. Krist, F. P. 383776, 1907; abst. J. S. C. I. 1908, **27,** 415. E. P. 24503, 1907; abst. J. S. C. I. 1908, **27,** 1033. C. Hagemann, E. P. 18470, 1891; abst. J. S. C. I. 1892, **11,** 1026. C. Hähnle, U. S. P. 1026577, 1912; abst. J. S. C. I. 1912, **31,** 584. W. Hall, E. P. 12502, 1888; abst. J. S. C. I. 1889, **8,** 814. U. S. P. 802754, 1905; abst. J. S. C. I. 1905, **24,** 1185. U. S. P. 802755, 1905; abst. J. S. C. I. 1905, **24,** 1185. R. Hamilton and I. C. Hamilton, E. P. 1433, 1889; abst. J. S. C. I. 1890, **9,** 211. W. Hancock and O. Dahl, Ber. 1895, 1588; J. S. C. I. 1895, **14,** 897. E. Hanausek, Ztschr. f. Nahrungmittelrentersuch u. Hygiene, 1887, **1,** 153; abst. J. S. C. I. 1887, **6,** 840. E. Hanausek and R. Zaloziecki, Chem. Ztg. 1905, **39,** 3–4; abst. J. S. C. I. 1905, **24,** 101. T. Hanausek, Papierfabrikant, 1911, **9,** 1464–1465; abst. J. S. C. I. 1911, **30,** 1446. W. Hargreaves,

—mainly nitrated—especially in Germany, a large portion of

Dept. Chem., S. Australia, Bull. No. 1, 1916, pp. 1–56; abst. J. S. C. I. 1917, **36**, 27. H. Havik, Papierfabrikant, 1912, **10**, 859–861; abst. J. S. C. I. 1912, **31**, 768. J. Heden, D. R. P. 212838, 1908; abst. J. S. C. I. 1909, **28**, 1001. W. Hellwig, U. S. P. 1121099, 1914; abst. J. S. C. I. 1915, **34**, 25. E. P. 28489, 1911; abst. J. S. C. I. 1912, **31**, 1075. F. P. 451957, 1912; abst. J. S. C. I. 1913, **32**, 653. D. R. P. 229390, 1909; abst. J. S. C. I. 1911, **30**, 278. W. Hellwig and F. Herrmann, E. P. 28489, 1911; abst. J. S. C. I. 1912, **31**, 1075. G. Herbein, F. P. 485771, 1918; abst. C. A. 1919, **13**, 1909. J. Hertkorn, Chem. Ztg. 1902, **26**, (55), 632; abst. J. S. C. I. 1902, **21**, 1041. L. Herz, E. P. 24131, 1908; abst. J. S. C. I. 1909, **28**, 1271. F. P. 397576, 1908; abst. J. S. C. I. 1909, **28**, 811. D. R. P. 220424, 1909; abst. J. S. C. I. 1910, **29**, 751. U. S. P. 1039941, 1912; abst. J. S. C. I. 1912, **31**, 1027. F. P. 422490, 1910; abst. J. S. C. I. 1911, **30**, 533. U. S. P. 1041791, 1912; abst. J. S. C. I. 1912, **31**, 1075. E. P. 25255, 1911 and 19334, 1912; abst. J. S. C. I. 1912, **31**, 1176. First addition dated Nov. 6, 1911, to F. P. 422490, 1910; J. S. C. I. 1911, **30**, 533; abst. J. S. C. I. 1912, **31**, 485. R. Herzog and F. Hörth, Z. Physiol. Chem. 1909, **60**, 152–154; Z. anal. Chem. 1896, **35**, 344; abst. J. S. C. I. 1909, **28**, 667. G. Heyl-Dia, E. P. 2610, 1899; abst. J. S. C. I. 1899, **18**, 602. G. Hibbert, E. P. 25040, 1894; abst. J. S. C. I. 1896, **15**, 291. E. P. 6897, 1887; abst. J. S. C. I. 1888, **7**, 398. A. Himzke, U. S. P. 702556, 1902; abst. J. S. C. I. 1902, **21**, 986. U. S. P. 1303314; abst. C. A. 1919, **13**, 1928. F. Hiorth, E. P. 15995, 1890; abst. J. S. C. I. 1891, **10**, 157. P. Hoering, E. P. 21328, 1911; abst. J. S. C. I. 1912, **31**, 1027. W. Hoffmeister, Landw. Jahrb. **17**, 239; abst. J. S. C. I. 1888, **7**, 620. H. Hoffmann, Papier Ztg. 1907, **32**, 2558; abst. J. S. C. I. 1907, **26**, 942. M. Holaubek, F. P. 353730, 1905; abst. J. S. C. I. 1905, **24**, 1079. T. Holmes, U. S. P. 704259, 1902; abst. J. S. C. I. 1902, **21**, 1093. M. Hönig, Chem. Ztg. 1912, **36**, 889–890; abst. J. S. C. I. 1912, **31**, 768. G. Horteloup, F. P. 327136, 1902; abst. J. S. C. I. 1903, **22**, 879. F. P. 331176, 1903; abst. J. S. C. I. 1903, **22**, 1145, 1146. E. P. 26149, 1903; abst. J. S. C. I. 1904, **23**, 266. E. P. 26150, 1903; abst. J. S. C. I. 1904, **23**, 500. W. Hoskins, U. S. P. 770463, 1904; abst. J. S. C. I. 1904, **23**, 990. U. S. P. 1226333, 1917; abst. J. S. C. I. 1917, **36**, 708. W. Hough, U. S. P. 903859, 1908; 931608, 1909; abst. J. S. C. I. 1908, **27**, 1212; 1909, **28**, 1148. F. P. 406514, 1909; abst. J. S. C. I. 1910, **29**, 483. G. C. Howard, U. S. P. 997064, 1911; abst. J. S. C. I. 1911, **30**, 951. U. S. P. 1057151, 1913; abst. J. S. C. I. 1913, **32**, 421. U. S. P. 1258568, 1918; abst. J. S. C. I. 1918, **37**, 264-A. E. P. 20220, 1911; abst. J. S. C. I. 1912, **31**, 812. C. Hudson and T. Harding, J. A. C. S. 1917, **39**, 1038–1040; abst. J. S. C. I. 1917, **36**, 730; J. A. C. S. 1918, **40**, 1601–1602; J. S. C. I. 1917, **36**, 730; abst. J. S. C. I. 1918, **37**, 778-A. E. Hudson and H. Merriam, U. S. P. 1303321, 1919; Appl. Feb. 7, 1917; abst. J. S. C. I. 1919, **38**, 494-A. Hughes, F. P. 320162, 1902; abst. J. S. C. I. 1903, **22**, 42; U. S. P. 691771; abst. J. S. C. I. 1902, **21**, 362. J. Hughes, U. S. P. 691770 and 691771, 1902; abst. J. S. C. I. 1902, **21**, 362. W. Huntington, U. S. P. 709488, 1902; abst. J. S. C. I. 1902, **21**, 1345. R. Hutchison, E. P. 7112, 1893; abst. J. S. C. I. 1893, **12**, 780. T. Hutchinson and United Railway and Trading Co., E. P. 20267, 1907; abst. J. S. C. I. 1909, **28**, 106. G. Huth and J. Bertram and Son, Ltd., E. P. 21962, 1899; abst. J. S. C. I. 1900, **19**, 370. A. Ihl, Chem. Ztg. 1890, **14**, 34, 67; abst. J. S. C. I. 1890, **9**, 418. E. Imhaus, F. P. 355245, 1905; abst. J. S. C. I. 1905, **24**, 1185. J. Irwin, U. S. P. 1250106, 1917; abst. J. S. C. I. 1918, **37**, 120-A. H. Jackson, U. S. P. 1083102 and 1083213, 1913; abst. J. S. C. I. 1914, **33**, 132. E. P. 25051, 1910; E. P. 6019, 1911; abst. J. S. C. I. 1912, **31**, 225. E. P. 4996, 1904; abst. J. S. C. I. 1905, **24**, 149. First addition (dated May 15, 1912) to F. P. 435090, 1911; abst. J. S. C. I. 1912, **31**, 1075. E. P. 12933, 1911; abst. J. S. C. I. 1912, **31**, 636.

which was first purified by solution in concentrated hydrochloric

S. Jacques, E. P. 30579, 1897; abst. J. S. C. I. 1898, **17,** 944. J. Jardine, U. S. P. 1143401, 1915; abst. J. S. C. I. 1915, **34,** 831. E. P. 18371, 1913; abst. J. S. C. I. 1914, **33,** 1006. J. Jardine and T. Nelson, F. P. 475981, 1914; abst. J. S. C. I. 1915, **34,** 1245. E. P. 18371, 1913; abst. J. S. C. I. 1914, **33,** 1006. Jensen and Son, E. P. 6831, 1900; abst. J. S. C. I. 1901, **20,** 602. S. Jentsch, Zts. ang. Chem. 1918, **31,** 72; abst. J. S. C. I. 1918, **37,** 365-A. B. Jirotka, D. R. P. 288320, 1914; abst. J. S. C. I. 1916, **35,** 542. E. P. 15105, 1911; abst. J. S. C. I. 1912, **31,** 67. B. Johnsen, Papierfabr. 1913, **11,** 979–980; abst. J. S. C. I. 1913, **32,** 863; abst. J. S. C. I. 1918, **37,** 129-T. J. Johnson, E. P. 5160, 1883; abst. J. S. C. I. 1884, **3,** 495. E. P. 7511, 1884; abst. J. S. C. I. 1885, **4,** 363. J. Johnson, E. P. 24503, 1893; abst. J. S. C. I. 1894, **13,** 1216. W. Johnson, U. S. P. 733969, 1903; abst. J. S. C. I. 1903, **22,** 961. G. Wildridge, E. P. 9517, 1900; abst. J. S. C. I. 1901, **20,** 603. E. Jones, U. S. P. 696822, 1902; abst. J. S. C. I. 1902, **21,** 635. A. Jouve, F. P. 359452, 1905; abst. J. S. C. I. 1906, **25,** 389. J. Juel and E. Ryan, E. P. 2349, 1891; abst. J. S. C. I. 1891, **10,** 566. P. Justice, E. P. 8983, 1903; abst. J. S. C. I. 1903, **22,** 1011. A. Kaiser, Chem. Ztg. 1902, **26,** (31), 355; abst. J. S. C. I. 1902, **21,** 725. A. Kalmann, E. P. 3656, 1901; abst. J. S. C. I. 1902, **21,** 422. W. Kershaw, E. P. 12682, 1896; abst. J. S. C. I. 1897, **16,** 696. F. Keyes, E. P. 4309, 1900; abst. J. S. C. I. 1901, **20,** 62. W. Keys, E. P. 1517, 1890; abst. J. S. C. I. 1890, **9,** 541. W. Kilby, Chem. Ztg. 1910, **34,** 1077–1078, 1091–1093; abst. J. S. C. I. 1910, **29,** 1265; Chem. Ztg. 1915, **39,** 212–214, 261–265, 284–285, 307–308, 350–352; J. S. C. I. 1910, **29,** 1052 (Wallin and Ekström); J. S. C. I. 1915, **34,** 275 (Landmark); J. S. C. I. 1913, **32,** 652; 1915, **34,** 274 (Strehlenert and Rinman); abst. J. S. C. I. 1915, **34,** 1085. A. Kirner, F. P. 353538, 1905; abst. J. S. C. I. 1905, **24,** 1028. E. P. 8206, 1905; abst. J. S. C. I. 1906, **25,** 132. F. P. first addn. dated Oct. 1905 to F. P. 353538 (J. S. C. I. 1905, **24,** 1028); abst. J. S. C. I. 1906, **25,** 388. J. Kitsee, U. S. P. 775829, 1904; abst. J. S. C. I. 1904, **23,** 1233. A. Klein, Paper-Making, 1907, **26,** 180–181; abst. J. S. C. I. 1907, **26,** 482; Papierfabrikant, 1914, **22,** 601–603, 634–636; J. S. C. I. 1910, **29,** 810, 1052, 1265; 1913, **32,** 652; 1914, **33,** 307; abst. J. S. C. I. 1914, **33,** 1201. P. Klemm, Wochenbl. Papierfabr. 1909, **40,** 3973–3976; abst. J. S. C. I. 1910, **29,** 16; Wochenbl. Papierfabr. 1911, **42,** 967–968; abst. J. S. C. I. 1911, **30,** 413. J. Klinsch, E. P. 15529, 1899; abst. J. S. C. I. 1900, **19,** 682. The Kellner-Partington Paper-Pulp Co., Ltd., E. P. 15783, 1895; abst. J. S. C. I. 1896, **15,** 668. A. Knopf, E. P. 13255, 1900; abst. J. S. C. I. 1901, **20,** 926. E. P. 13269, 1902; abst. J. S. C. I. 1903, **22,** 646. E. Kolb, D. R. P. 189882, 1905; abst. J. S. C. I. 1908, **27,** 244. L. Kollmann, Papierfabrikant, 1911, **9,** 845–851; abst. J. S. C. I. 1911, **30,** 949. C. Kollner, E. P. 20225, 1891; abst. J. S. C. I. 1893, **12,** 461. H. Krause, Chem. Ind. 1906, **29,** 217–227; abst. J. S. C. I. 1906, **25,** 493. O. Kress, J. I. E. C. 1916, **8,** 883–886; abst. J. S. C. I. 1916, **35,** 1105. O. Kress and C. Textor, J. I. E. C. 1918, **10,** 268–270; abst. J. S. C. I. 1918, **37,** 296-A. O. Kress and S. Wells, U. S. P. 1266957, 1918; abst. J. S. C. I. 1918, **37,** 543-A. R. Kron, E. P. 2560, 1910; abst. J. S. C. I. 1911, **30,** 80. F. P. 381462, 1907; abst. J. S. C. I. 1908, **27,** 178. V. Kuess, E. P. 20911, 1909; abst. J. S. C. I. 1910, **29,** 1053. F. P. 394494, 1908; abst. J. S. C. I. 1909, **28,** 257. E. P. 29480, 1909; abst. J. S. C. I. 1910, **29,** 751. F. P. 409614, 1909; abst. J. S. C. I. 1910, **29,** 752. A. Kuhn, Papierfabr. 1914, **11,** Fest-heft, 53–60; abst. J. S. C. I. 1914, **33,** 744. C. Kurtz-Hähnle, E. P. 26019, 1911; abst. J. S. C. I. 1912, **31,** 1176; U. S. P. 1026577, 1912; abst. J. S. C. I. 1912, **31,** 584. W. Ladd and M. Keen, U. S. P. Re. 1449, 1863. S. Lagermarck and W. Sverdrup, U. S. P. 1161696, 1915; abst. J. S. C. I. 1916, **35,** 39. H. Lake, E. P. 7774, 1902; abst. J. S. C. I. 1903, **22,** 646; E. P. 210, 1896; abst. J. S. C. I. 1897, **16,** 630; E. P. 20145, 1892; abst. J. S. C. I. 1893, **12,** 462;

acid by the process of Wilstaetter, as detailed on page 93.

E. P. 11484, 17227, 1888; abst. J. S. C. I. 1888, **7,** 864; 1889, **8,** 209; E. P. 1808, 1887; abst. J. S. C. I. 1887, **6,** 380; E. P. 15188, 1884; abst. J. S. C. I. 1885, **4,** 243; E. P. 6376, 1884; abst. J. S. C. I. 1884, **3,** 496. W. Lake, E. P. 6534, 1901; abst. J. S. C. I. 1902, **21,** 362; E. P. 12346, 1884; abst. J. S. C. I. 1885, **4,** 242. U. S. P. 683836; abst. J. S. C. I. 1902, **21,** 64. L. Langville, U. S. P. 475062, 1892. E. P. 13847, 1892; abst. J. S. C. I. 1892, **11,** 935; E. P. 18519, 1893; abst. J. S. C. I. 1894, **13,** 170. A. Lannoye, E. P. 7872, 1913; abst. J. S. C. I. 1914, **33,** 132. F. P. 457006, 1913; abst. J. S. C. I. 1913, **32,** 1063. C. Lee, U. S. P. 701271, 1902; abst. J. S. C. I. 1902, **21,** 1092. A. Lefebvre, U. S. P. 1277737, 1918; abst. J. S. C. I. 1918, **37,** 687-A. Legrand, Papierfabrikant, 1910, **9,** 32–33; abst. J. S. C. I. 1910, **29,** 208. Lehmann, Papier Ztg. 1904, **29,** 3562; abst. J. S. C. I. 1904, **23,** 1233. J. Lester, J. S. C. I. 1902, **21,** 380; abst. J. S. C. I. 1905, **24,** 171. G. Lightfoot, Advisory Council of Sci. and Ind., Bull. No. 11, 1919; J. S. C. I. 1917, **36,** 27; abst. J. S. C. I. 1919, **38,** 356-A. J. Lindsey and B. Tollens, Ann. **267,** 341; Landw. Vers.-Sta. **13,** 222; Chem. Soc. J. **55,** 213; J. S. C. I. 1892, **11,** 835; Zts. ang. Chem. 1892, 154–158; abst. J. S. C. I. 1893, **12,** 287. V. Litchauer, Centr. für oesterr. Papier Industrie, 1918, **23;** Paper, 1919, **23,** 646–52; abst. C. A. 1919, **13,** 1016. A. Little, Amer. Inst. Chem. Eng., Jan. 12, 1912; Met. and Chem. Eng. 1916, **14,** 133–135; J. S. C. I. 1914, **33,** 71; U. S. P. 1092221, 1914; J. S. C. I. 1914, **33,** 477, 563; abst. J. S. C. I. 1916, **35,** 301. L. Litynski, A. Rodakiewiez and F. Kurowski, E. P. 16996, 1898; abst. J. S. C. I. 1899, **18,** 763. F. Long, U. S. P. 702142, 1902; abst. J. S. C. I. 1902, **21,** 986. E. P. 3178, 1902; J. S. C. I. 1902, **21,** 1092. W. Longley, E. P. 19250, 1905; abst. J. S. C. I. 1906, **25,** 845. J. Lorimer, E. P. 16765, 1886; abst. J. S. C. I. 1887, **6,** 508; E. P. 16780, 1886; abst. J. S. C. I. 1887, **6,** 508. J. Lundberg, U. S. P. 1257290, 1918; abst. J. S. C. I. 1918, **37,** 238-A. D. R. P. 284628, 1914; abst. J. S. C. I. 1915, **34,** 1048. A. Luttringer, Papierfabr. 1913, **11,** 884–886; abst. J. S. C. I. 1913, **32,** 822. P. Magnier and A. Brangier, E. P. 12241, 1899; abst. J. S. C. I. 1900, **19,** 165. U. S. P. 695573, 1902; abst. J. S. C. I. 1902, **21,** 632. J. Makin, E. P. 5626, 1885; abst. J. S. C. I. 1891, **10,** 157. N. Malcolmson, E. P. 28163, 1908; abst. J. S. C. I. 1910, **29,** 147. G. Mallary, E. P. 8862, 1887; abst. J. S. C. I. 1888, **7,** 639. C. Marchand, U. S. P. 1155256, 1915; abst. J. S. C. I. 1915, **34,** 1087. E. Marks, E. P. 123111, 1917; abst. J. S. C. I. 1919, **38,** 216-A. R. Marr, U. S. P. 1166848, 1916; abst. J. S. C. I. 1916, **35,** 250. M. Marsden, U. S. P. 781612, 1905; abst. J. S. C. I. 1905, **24,** 208; U. S. P. 1165689, 1915; abst. J. S. C. I. 1916, **35,** 250. G. Marshall, U. S. P. 982379, 1911; abst. J. S. C. I. 1911, **30,** 278. H. Martinson, U. S. P. 708058, 1902; abst. J. S. C. I. 1902, **21,** 1345. T. Marusawa, U. S. P. 1244525, 1917; abst. J. S. C. I. 1918, **37,** 6-A. A. Masson and R. Scott, E. P. 26501, 1898; abst. J. S. C. I. 1899, **18,** 1150. H. Maste, U. S. P. 480334, 1892; J. A. C. S. 1892, **14,** 297. Matheus, Papierfabr. 1911, **9,** 1375–1376; abst. J. S. C. I. 1911, **30,** 1374; Papierfabr. 1911, **9,** 93–95; abst. J. S. C. I. 1911, **30,** 204. J. Mathieu, E. P. 2767, 1899; abst. J. S. C. I. 1900, **19,** 370. H. Mayr, Handbuch der Papierfabr. (4), 1896, 1592–96; abst. J. S. C. I. 1896, **15,** 468. H. McCormack and E. McMullen, U. S. P. 1196708, 1916; abst. J. S. C. I. 1916, **35,** 1009. A. McDougall, E. P. 4569, 1885; abst. J. S. C. I. 1886, **5,** 676. I. McDougall, E. P. 1349 and 3257, 1883; abst. J. S. C. I. 1888, **7,** 451. J. T. M'Dougall, E. P. 3257, 1883; abst. J. S. C. I. 1884, **3,** 190. J. T. and J. M'Dougall, E. P. 1795, 1886; abst. J. S. C. I. 1887, **6,** 146. J. McLaughlin, U. S. P. 706441, 1902; abst. J. S. C. I. 1902, **21,** 1150. A. McQuade, E. P. 26811, 1898; abst. J. S. C. I. 1899, **18,** 392. W. McRae, U. S. P. 1151490, 1915; abst. J. S. C. I. 1915, **34,** 1008. E. P. 26043, 1911; abst. J. S. C. I. 1912, **31,** 769. W. McRae and N. Malcolmson, E. P. 26043, 1911; abst. J. S. C. I. 1912, **31,** 769; E. P. 14871, 1911; abst. J. S.

Either the wood pulp was first made into paper—as in the

C. I. 1912, **31**, 769; F. P. 452989, 1912; abst. J. S. C. I. 1913, **32**, 748. Meister, Lucius and Brüning, F. P. 373182, 1906; abst. J. S. C. I. 1907, **26**, 606. E. P. 5342, 1906; abst. J. S. C. I. 1907, 317. J. Melchers, U. S. P. 1162797, 1915; abst. J. S. C. I. 1916, **35**, 108. C. Melhardt, D. R. P. 279102 1913; abst. J. S. C. I. 1915, **34**, 276. R. Menzies, U. S. P. 714216, 1902; abst. J. S. C. I. 1903, **22**, 42; E. P. 28, 1902; abst. J. S. C. I. 1903, **22**, 109. J. Merrill, U. S. P. 1145498, 1915; abst. J. S. C. I. 1915, **34**, 867. R. Menzies, C. Cross and J. Bevan, E. P. 6840, 1885; abst. J. S. C. I. 1886, **5**, 321. E. Millard, U. S. P. 1244116, 1917; abst. J. S. C. I. 1918, **37**, 6-A. M. Mills, U. S. P. 729953, 1903; abst. J. S. C. I. 1903, **22**, 817. S. Milne, E. P. 14070, 1914; abst. J. S. C. I. 1915, **34**, 867; E. P. 2420, 1903; abst. J. S. C. I. 1904, **23**, 335; E. P. 28611, 1903; abst. J. S. C. I. 1905, **24**, 102. F. P. 478063, 1915; abst. J. S. C. I. 1916, **35**, 1106. C. Milts, U. S. P. 691958; abst. J. S. C. I. 1902, **21**, 362. A. Monin, F. P. 366112, 1906; abst. J. S. C. I. 1906, **25**, 1064. K. Monroe, J. A. C. S. 1919, **41**, 1002–1003. LaForge and Hudson, J. S. C. I. 1919, **38**, 86-A; Hudson and Harding, J. S. C. I. 1918, **37**, 778-A; abst. J. S. C. I. 1919, **38**, 550-A. Montanus, Wochenbl. Papierfabr. 1904, **35**, 2832–3; abst. J. S. C. I. 1904, **23**, 947. H. de Montessus, Papier Ztg. 1907, **32**, 1534–5; abst. J. S. C. I. 1907, **26**, 633. H. de Montessus de Ballore, F. P. 322921, 1902; abst. J. S. C. I. 1903, **22**, 437. G. Moore, U. S. P. 1207978, 1916; abst. J. S. C. I. 1917, **36**, 132. O. Moore, U. S. P. 695754, 1902; abst. J. S. C. I. 1902, **21**, 635. W. Moore, E. P. 118291, 1917; abst. J. S. C. I. 1918, **37**, 575-A. K. Mörch, U. S. P. 1160942, 1915; abst. J. S. C. I. 1915, **34**, 1245. E. Morterud, U. S. P. 883328, 1908; abst. J. S. C. I. 1908, **27**, 466; U. S. P. 1299597, 1919; abst. J. S. C. I. 1919, **38**, 459-A; D. R. P. 286074, 1913; abst. J. S. C. I. 1916, **35**, 173. M. Müller and O. Heigis, D. R. P. 284681, 1914; abst. J. S. C. I. 1915, **34**, 1048. L. deNaeyer, E. P. 12461, 1895; abst. J. S. C. I. 1896, **15**, 554. D. Nagy, D. R. P. 180847, 1905; abst. J. S. C. I. 1907, **26**, 1064. W. Nanson, Paper-making, 1916, **35**, 371–374; abst. J. S. C. I. 1917, **36**, 131. B. Nase, U. S. P. 1061316, 1913; abst. J. S. C. I. 1913, **32**, 652. T. Nash, U. S. P. 1140181, 1915; abst. J. S. C. I. 1915, **34**, 656. E. P. 6876, 1914; abst. J. S. C. I. 1914, **33**, 640. A. Navarre, Ind. Electrochim. 1890, **3**, 49–51; abst. J. S. C. I. 1900, **19**, 267. P. Nebrich, E. P. 16403, 1904; abst. J. S. C. I. 1904, **23**, 949. F. P. 345827, 1904; abst. J. S. C. I. 1905, **24**, 40. J. Nef, O. F. Hedenburg and J. W. E. Glattfield, J. A. C. S. 1917, **39**, 1683–1652 (see J. S. C. I. 1908, **27**, 31; 1910, **29**, 1264); abst. J. S. C. I. 1917, **36**, 1022. J. Neil, F. P. 442850, 1912; abst. J. S. C. I. 1912, **31**, 1027. E. Nemethy, F. P. 373721, 1906; abst. J. S. C. I. 1907, **26**, 713. M. Nerson, F. P. 403023, 1908; abst. J. S. C. I. 1909, **28**, 1323. A. Neuberger, Papier Ztg. 1903, **27**, (3), 70–71; abst. J. S. C. I. 1903, **22**, 159. E. Neubauer, Zts. ang. Chem. 1912, **25**, 2155–2159; abst. J. S. C. I. 1912, **31**, 1026. A. Newell and R. J. Marx, E. P. 2865, 1915; abst. J. S. C. I. 1915, **34**, 1138; F. P. 477995, 1915; abst. J. S. C. I. 1916, **35**, 1009. P. Newton, E. P. 2046, 1888; abst. J. S. C. I. 1889, **8**, 209. E. Nickel, Chem. Ztg. 1883, **17**, 1209; abst. J. S. C. I. 1893, **12**, 869; Chem. Ztg. 1883, **17**, 869; J. S. C. I. 1893, **12**, 869; abst. J. S. C. I. 1894, **13**, 423. H. Nishida, J. I. E. C. 1916, **8**, 1096–1100; abst. J. S. C. I. 1917, **36**, 27. Nodon, Bretonneau, and D'Alton-Shee, Rev. Prod. Chim. **1**, (13), 196; abst. J. S. C. I. 1899, **18**, 63. le Normant des Varnnes and A. Regmouf de Vains, F. P. 347925, 1904; abst. J. S. C. I. 1905, **24**, 454; U. S. P. 818206, 1906; abst. J. S. C. I. 1906, **25**, 494. E. P. 505, 1905; abst. J. S. C. I. 1906, **25**, 494. V. Nunez, Papierfabr. 1914, **12**, Fest-heft, 41–44; abst. J. S. C. I. 1914, **33**, 744. J. Nussbaum and W. Ebert, Papierfabr. 1907, Parts 24 and 25; abst. J. S. C. I. 1907, **26**, 1063. F. Oliver, Brit. Med. Jour., April 13, 1918; abst. J. S. C. I. 1918, **37**, 246-R. D. Otto, E. P. 11651, 1884; abst. J. S. C. I. 1885, **4**, 415. H.

method of the Westphalische Anhaltische Sprengstoff Aktiengessel-

Parker, E. P. 5219, 1906; abst. J. S. C. I. 1907, **26,** 220. F. P. 365866, 1906; abst. J. S. C. I. 1906, **25,** 1001. E. P. 22718, 1905; abst. J. S. C. I. 1906, **25,** 232; E. P. 76, 1902; abst. J. S. C. I. 1902, **21,** 870. U. S. P. 808614, 1905; abst. J. S. C. I. 1906, **25,** 88; U. S. P. 693896, 1902; abst. J. S. C. I. 1902, **21,** 494. von Possanner, Papierfabr., Fest und Auslandsheft, 1912, **10,** 60–1; abst. J. S. C. I. 1912, **31,** 713. R. Pearson, abst. J. S. C. I. 1917, **36,** 631. R. Pearson and J. S. Stoneham, E. P. 26573, 1908; abst. J. S. C. I. 1910, **29,** 17. N. Pederson, E. P. 119028, 1918; abst. J. S. C. I. 1919, **38,** 760-A. V. de Perini, F. P. 370547, 1906; abst. J. S. C. I. 1907, **26,** 252; U. S. P. 831521, 1906; abst. J. S. C. I. 1906, **25,** 1040; E. P. 20005, 1906; abst. J. S. C. I. 1907, **26,** 1087. S. Persichetti, F. P. 318650, 1902; abst. J. S. C. I. 1902, **21,** 1467. J. Persoz, Rev. Gen. Mat. Col. 1911, **15,** 40–3; abst. J. S. C. I. 1911, **30,** 278. L. Peufaillit, first addition dated Jan. 31, 1911 to F. P. 413097, 1910; abst. J. S. C. I. 1912, **31,** 428. E. P. 22869, 1910; abst. J. S. C. I. 1911, **30,** 1307. F. P. 413097, 1910; abst. J. S. C. I. 1910, **29,** 1101. L. Peufaillit and A. Leblanc, F. P. 415188, 1910; abst. J. S. C. I. 1910, **29,** 1245. H. Pfeifer, E. P. 27587, 1903; abst. J. S. C. I. 1905, **24,** 149; F. P. 338330, 1903; abst. J. S. C. I. 1904, **23,** 620. J. Pfiel, U. S. P. 1058898, 1913; abst. J. S. C. I. 1913, **32,** 531. F. P. 431044, 1911; abst. J. S. C. I. 1911, **30,** 1375. S. Phillips, J. Soc. Arts, 1905, **53,** 700–717; abst. J. S. C. I. 1905, **24,** 633. S. Pitt, E. P. 9509, 1884; abst. J. S. C. I. 1885, **4,** 464. Poore, B. Appl. 17278, July 15; J. S. C. I. 1919, **38,** 557-A. von Possanner, Wochenbl. Papierfabr. 1911, **42,** 1157–8; J. S. C. I. 1911. **30,** 278; abst. J. S. C. I. 1911, **30,** 483. R. Preston and T. Thornley, E. P. 2743, 1894; abst. J. S. C. I. 1895, **14,** 183. P. Priem, U. S. P. 997144, 1908; abst. J. S. C. I. 1908, **27,** 1220. W. Raitt, E. P. 16488, 1915; abst. J. S. C. I. 1916, **35,** 1009; E. P. 15779, 1912; abst. J. S. C. I. 1913, **32,** 785. F. P. 453307, 1913; abst. J. S. C. I. 1913, **32,** 785; Paper-making, 1907, **24,** 505–508, 539–541; abst. J. S. C. I. 1908, **27,** 35; Indian Forest Reports, 1912, **3,** Part 3, 1–37; J. S. C. I. 1912, **31,** 870; abst. J. S. C. I. 1912, **31,** 1025; Eighth Int. Cong. Appl. Chem. 1912, Sect. VI^{a} Orig. Comm. **13,** 219–232; abst. J. S. C. I. 1912, **31,** 870. C. Ramsey, E. P. 1834, 1889; abst. J. S. C. I. 1890, **9,** 211. G. Rayner, F. P. 453307, 1912; abst. J. S. C. I. 1913, **32,** 785. H. Reed, U. S. P. 1310713, 1919; abst. C. A. 1919, **13,** 2443. J. Readmann and G. Gemmell, abst. J. S. C. I. 1893, **12,** 1005; Chem. Tr. J., July 22, 1893, 51. R. Redmayne, E. P. 927, 1891; abst. J. S. C. I. 1892, **11,** 176. T. Reid, abst. J. S. C. I. 1886, **5,** 273, 349; E. P. 9774, 1884; abst. J. S. C. I. 1885, **4,** 507. P. Reinicke, F. P. 388748, 1908; abst. J. S. C. I. 1908, **27,** 956. J. Remington, D. A. Bowack and P. W. Davidson, Aynsome Annual, 1911, **3,** 5–11; World's Paper Trade Rev. 1911; abst. J. S. C. I. 1912, **31,** 582. J. Remington, D. Bowack and B. Dixon, World's Paper Trade Review, 1909, **51,** 6–8; abst. J. S. C. I. 1909, **28,** 540. G. Richmond, Philipp. J. Sci. 1906, **1,** 433–462; abst. J. S. C. I. 1906, **25,** 863; Philipp. J. Sci. 1906, **1,** 1075–1084; abst. J. S. C. I. 1907, **26,** 274; Philipp. J. Sci. 1910, **5,** 233–255. Sindall, J. S. C. I. 1907, 1157. Raitt, J. S. C. I. 1908, **27,** 35; J. S. C. I. 1906, **25,** 863; 1907, **26,** 274, 941; abst. J. S. C. I. 1910, **29,** 1450. B. Roberts, Appl. 17547, July 14; J. S. C. I. 1919, **38,** 557-A. C. Roberts, U. S. P. 954209, 1910; abst. J. S. C. I. 1910, **29,** 556. R. Roe, U. S. P. 783137, 1905; abst. J. S. C. I. 1905, **24,** 288. F. Roeckner and R. Roeckner, E. P. 9126, 1892; abst. J. S. C. I. 1893, **12,** 461. H. Rogers, E. P. 19376, 1890; abst. J. S. C. I. 1891, **10,** 1022. W. Ruth, U. S. P. 781097, 1905; abst. J. S. C. I. 1905, **24,** 208. R. Ruttin, J. S. C. I. 1898, **17,** 365, 481, 1164; 1900, **19,** 1028; 1901, **20,** 734, 1008; abst. J. S. C. I. 1909, **28,** 1290. C. Sahlström and E. Parr, E. P. 14943, 1892; abst. J. S. C. I. 1893, **12,** 825. Sandberg and G. K. Sundblad, E. P. 24125, 1912; abst. J. S. C. I. 1913, **32,** 279. H. Sanguinetti, E. P. 16245, 1904; abst. J. S. C. I. 1905, **24,** 855.

schaft—and after tearing into small pieces was nitrated in centri-

H. Sanguinetti and P. H. Sanguinetti, E. P. 9682, 1898; abst. J. S. C. I. 1899, **18**, 602. E. Savage, U. S. P. 710014, 1902; abst. J. S. C. I. 1902, **21**, 1345. B. Saylor, U. S. P. 1004473, 1911; abst. J. S. C. I. 1911, **30**, 1207. F. P. 428678, 1911; abst. J. S. C. I. 1911, **30**, 1156. O. Schmidt, Papier Ztg. 1901, **26**, (13), 475–477; abst. J. S. C. I. 1901, **20**, 382. H. Schmolka, E. P. 21222, 1900; abst. J. S. C. I. 1901, **20**, 496. L. Schopper, E. P. 27948, 1907; abst. J. S. C. I. 1908, **27**, 588. E. Schreiber, D. R. P. 197983, 1907; abst. J. S. C. I. 1908, **27**, 708. F. Schreyer, F. P. 431044, 1911; abst. J. S. C. I. 1911, **30**, 1375. R. Schuehmacher, F. P. 373327, 1907; abst. J. S. C. I. 1907, **26**, 713. E. Schuricht, D. R. P. 20139, 1882 (addn. to D. R. P. 5427, 1878); abst. J. S. C. I. 1883, **2**, 188. C. Schwalbe, Verein deut. Chem. Sep. 1918; Zts. ang. Chem. 1918, **31**, 193–4; abst. J. S. C. I. 1918, **37**, 685-A. G. Sellergen, Paper-Making, 1907, **26**, 231; abst. J. S. C. I. 1907, **26**, 633. W. Sembritzki, Papier Ztg. 1908, **33**, 872; abst. J. S. C. I. 1908, **27**, 466. D. Sharpe, U. S. P. 694678, 1902; abst. J. S. C. I. 1902, **21**, 494. C. Shartle, U. S. P. 1173748, 1916; abst. J. S. C. I. 1916, **35**, 465. J. Shorrock, E. P. 15956, 1888; abst. J. S. C. I. 1889, **8**, 914. H. Simonin, F. P. 407844, 1909; abst. J. S. C. I. 1910, **29**, 647. J. Simons and S. Smith, E. P. 10259, 1890; abst. J. S. C. I. 1891, **10**, 566. G. Sinclaire, E. P. 6441, 1893; abst. J. S. C. I. 1893, **12**, 779. R. Sindall, abst. J. S. C. I. 1918, **37**, 167-R; Report to Indian Govt., Rangoon, March, 1906; abst. J. S. C. I. 1907, **26**, 1157; Pamphlet 1900, 1–15; abst. J. S. C. I. 1900, **19**, 843. Readmann and Gemell, J. S. C. I. 1893, **12**, 1005; J. S. C. I. 1896, **15**, 239. M. Singer, Dingler, **246**, 487; 1879, **233**, 413; abst. J. S. C. I. 1883, **2**, 89. E. Slack, Techn. Committee Canadian Paper and Pulp Assoc.; Pulp and Paper Mag. 1919, **17**, 265–270; abst. J. S. C. I. 1919, **38**, 356-A. B. Smärt, Papier Ztg. 1909, **34**, 923–924; abst. J. S. C. I. 1909, **28**, 438. A. Smith, abst. J. S. C. I. 1916, **35**, 281. W. Smith, E. P. 19150, 1909; abst. J. S. C. I. 1910, **29**, 1152. Soc. Anon. Le Camphre, F. P. 462681, 463879, 1912; abst. J. S. C. I. 1914, **33**, 430; Soc. anon. "Mirabet," F. P. 355852, 1905; abst. J. S. C. I. 1905, **24**, 1252. Soc. anon. pour la Fab. des Pates a Papier de lin et succedanes, F. P. 365046, 1906; abst. J. S. C. I. 1906, **25**, 950. Soc. Haemers et van Den Baviers, first addition dated Aug. 31, 1906 to F. P. 373668, March, 1906, J. S. C. I. 1907, **26**, 713; abst. J. S. C. I. 1907, **26**, 775; F. P. 373668, 1906, abst. J. S. C. I. 1907, **26**, 713. C. Solbrig, Papier Ztg. 1906, **31**, 3770; abst. J. S. C. I. 1907, **26**, 338. I. Söraas, U. S. P. 1297028, 1919; abst. J. S. C. I. 1919, **38**, 358-A; U. S. P. 1268774, 1918; abst. J. S. C. I. 1918, **37**, 543-A. H. Spicer, E. P. 120086, 1917 (appl. 15467, 1917); abst. J. S. C. I. 1919, **38**, 8-A. C. Springer, E. P. 8073, 1885; abst. J. S. C. I. 1886, **5**, 435. O. Stafford, E. P. 119040, 1918 (appl. 14708/18), Int. Conv. Sept. 10, 1917; abst. J. S. C. I. 1919, **38**, 215-A. O. Stage, U. S. P. 1279604, 1918; appl. 14318; abst. J. S. C. I. 1919, **38**, 8-A. N. Statham, U. S. P. 1298594, 1919; J. S. C. I. 1919, **38**, 459-A. F. Stehle, E. P. 10716, 1895; abst. J. S. C. I. 1896, **15**, 371. A. Steinschneider, Zts. ang. Chem. 1909, **22**, 1410–1411; J. S. C. I. 1909, **28**, 324; abst. J. S. C. I. 1909, **28**, 904. A. Stern. Proc. Chem. Soc. 1894, (142), 186–187-P; abst. J. S. C. I. 1894, **13**, 1230. C. Steward, H. D. Hall and H. Beadle, E. P. 116005, 1917; abst. J. S. C. I. 1918, **37**, 409-A. W. Stocks, E. P. 25393, 1910; abst. J. S. C. I. 1911, **30**, 1375. W. Stone and W. H. Test, Amer. Chem. J. 1893, **15**, 195; J. S. C. I. 1890, **9**, 748; abst. J. S. C. I. 1893, **12**, 618. J. Strachan, abst. J. S. C. I. 1919, **38**, 102-R. E. Strange, J. H. Carle and A. A. Longsdon, E. P. 27738, 1903; abst. J. S. C. I. 1904, **23**, 1207. E. Streeb, Mitth. aus den k. tech. Versuchstat. zu Berlin, 1893, **11**, 23; abst. J. S. C. I. 1893, **12**, 1053. F. Stromer, D. R. P. 21398, 1882; abst. J. S. C. I. 1883, **2**, 295. A. Stutzer, Wochenbl. Papierfabr. 1911, **42**, 4956; abst. J. S. C. I. 1912, **31**, 121; Chem. Ztg. 1910, **34**, 1352; J. S. C. I. 1909, **28**, 1162; abst. J. S. C. I. 1911, **30**, 18; Zts. ang. Chem. 1909, **22**, 1999–2005;

fugals, or else was purified by solution in HCl, extruded through

abst. J. S. C. I. 1909, **28,** 1162. H. E. Surface, U. S. Dept. Agric. Bull. No. 80, Aug. 31, 1914, 1–63; abst. J. S. C. I. 1914, **33,** 1151. H. Surface and R. E. Cooper, U. S. Dept. Agric. Bull. No. 72, May 29, 1914, 1–26; abst. J. S. C. I. 1914, **33,** 857. E. Sutermeister, Pulp and Paper Mag. 1919, **17,** 215–218, 243–246, 263–264, 289–292; abst. J. S. C. I. 1919, **38,** 356-A; Eighth Int. Cong. Appl. Chem. 1912, Sect. VI^a Orig. Comm. **13,** 265–69; abst. J. S. C. I. 1912, **31,** 869; Papierfabr. 1914, **12,** 898–900; abst. J. S. C. I. 1914, **33,** 857. H. Tartar, J. Ind. Eng. Chem. 1916, **8,** 226–228; Ekstroms, J. S. C. I. 1910, **29,** 810; abst. J. S. C. I. 1916, **35,** 483. C. Taylor and H. K. Cook, U. S. P. 1181553, 1916; abst. J. S. C. I. 1916, **35,** 686. C. Tennant-Lee, F. P. 345632, 1904; abst. J. S. C. I. 1905, **24,** 40. J. Thickens, U. S. Dept. of Forests Bull.; Papierfabr. 1914, **12,** 275-281; abst. J. S. C. I. 1914, **33,** 1202. W. Thompson, E. P. 18169, 1890; abst. J. S. C. I. 1892, **11,** 175. W. Thörner, Zts. Unters. Nahr. und Genussmittel, 1902, **5,** (7), 304–305; abst. J. S. C. I. 1902, **21,** 641. E. Tillberg, F. P. 385270, 1907; abst. J. S. C. I. 1908, **27,** 634. O. Tingberg, E. P. 6491, 1912; abst. J. S. C. I. 1912, **31,** 812. J. Tompkins, E. P. 3472, 1886; J. S. C. I. 1886, **5,** 435. T. Torrance and J. Hervell, E. P. 13587, 1893; abst. J. S. C. I. 1893, **12,** 946. H. Turner, U. S. P. 772192, 1904; abst. J. S. C. I. 1904, **23,** 1110. W. Umpherston, E. P. 13024, 1892; abst. J. S. C. I. 1893, **12,** 461. E. Valenta, Chem. Ztg. 1904, **28,** 502–503; abst. J. S. C. I. 1904, **23,** 686. J. Van Wessem, E. P. 117086, 1918; abst. J. S. C. I. 1919, **38,** 496-A. F. Veitch and J. L. Merrill, U. S. Dept. Bureau of Chem., Bull. No. 159, Jan. 18, 1913, 28 pp.; abst. J. S. C. I. 1913, **32,** 358. H. Vessier and A. Wilbaux, E. P. 14859, 1884; abst. J. S. C. I. 1885, **4,** 686. L. Vidal, Papierfabr. 1910, **8,** 1042–1045; abst. J. S. C. I. 1910, **29,** 1298. J. Vogel, Papierfabr. 1911, **9,** 438–440; abst. J. S. C. I. 1911, **30,** 532; Papier Ztg. 1907, **32,** 961–962; 1010–1012, 1054, 1098–1099; see also J. S. C. I. 1906, **25,** 555; abst. J. S. C. I. 1907, **26,** 482. N. Vrooman and R. Kirkland, U. S. P. 689934, 1901; abst. J. S. C. I. 1902, **21,** 271; U. S. P. 703682, 1902; abst. J. S. C. I. 1902, **21,** 1036. P. Waentig and W. Gierisch, Zts. ang. Chem. 1919, **32,** 173–175; J. S. C. I. 1913, **32,** 822; abst. J. S. C. I. 1919, **38,** 530-A. A. Wahlström, U. S. P. 771403, 1904; abst. J. S. C. I. 1904, **23,** 1041. C. Waite and J. E. Heden, U. S. P. 1249287, 1917; abst. J. S. C. I. 1918, **37,** 53-A. G. Walker, abst. J. S. C. I. 1911, **30,** 934. W. Walker, abst. J. S. C. I. 1913, **32,** 389. R. Wallace and G. Reynaud, F. P. 394234, 1907; abst. J. S. C. I. 1909, **28,** 255. J. Wallberg and J. Ullgren, E. P. 2685, 1896; abst. J. S. C. I. 1896, **15,** 372. G. Walsh, Paper-Making, 1917, **36,** 283–285; abst. J. S. C. I. 1917, **36,** 1091. J. Walton, E. P. 16113, 1886; abst. J. S. C. I. 1887, **6,** 223. H. Wandrowsky, D. R. P. 309630, 1918; abst. J. S. C. I. 1919, **38,** 283-A. J. Warren and F. A. Cloudman, E. P. 11610, 1887; abst. J. S. C. I. 1887, **6,** 736. R. Wasicky, Papierfabrikant, 1918, **16,** 212–213; Zts. ang. Chem. 1918, **31,** Ref. 371; abst. J. S. C. I. 1919, **38,** 131-A. H. Watson and J. S. Watson, E. P. 16928, 1890; abst. J. S. C. I. 1891, 944. D. Wells, J. I. E. C. 1913, **5,** 906–907; abst. J. S. C. I. 1913, **32,** 1102; U. S. P. 1269350, 1918; abst. J. S. C. I. 1918, **37,** 575-A; U. S. P. 1268193, 1918; abst. J. S. C. I. 1918, **37,** 453-A. W. Wentworth and A. B. Larchar, U. S. P. 912339 and 912340, 1909; abst. J. S. C. I. 1909, **28,** 541. F. Werle, E. P. 16281, 1904; abst. J. S. C. I. 1905, **24,** 40. Van Wessen, E. P. 122812, June 25 (10681, 1918); abst. J. S. C. I. 1919, **38,** 484-A. A. Westad and E. Häag, U. S. P. 1309267, 1919; abst. J. S. C. I. 1919, **38,** 678-A. C. Weygang, E. P. 12299, 1891; abst. J. S. C. I. 1892, **11,** 711-A. A. Wheeler, Ber. 1905, **38,** 2168–69; abst. J. S. C. I. 1905, **24,** 748; Ber. 1907, **40,** 1888–1890; abst. J. S. C. I. 1907, **26,** 633. A. White, U. S. P. 1197983, 1916; abst. J. S. C. I. 1916, **35,** 1106. A. White and J. Rue, Tech. Assoc. of Pulp and Paper Ind. N. Y., Feb. 7, 1917; Met. and Chem. Eng. 1917, **16,** 182–186; abst. J. S. C. I. 1917, **36,** small orifices into water as the precipitating medium, and these

383. J. White, E. P. 24381, 1901; abst. J. S. C. I. 1902, **21**, 493; E. P. 3091, 1899; abst. J. S. C. I. 1900, **19**, 370. E. P. 17022, 1891; abst. J. S. C. I. 1892, **11**, 935. Widsoe and Tollens, Ber. 1900, **33**, (1), 132–143; abst. J. S. C. I. 1900, **19**, 160. H. Wigger, E. P. 14563, 1889; abst. J. S. C. I. 1890, **9**, 819. M. Wilbuschewitsch, E. P. 27950, 1909; abst. J. S. C. I. 1911, **30**, 80. F. Williams, abst. J. S. C. I. 1913, **32**, 457. B. Williamson, U. S. P. 1025356, 1912; abst. J. S. C. I. 1912, **31**, 532. I. Willstätter and L. Zechmeister, Ber. 1913, **46**, 2401–2412; abst. J. S. C. I. 1913, **32**, 822. F. Wolesky, Papier Ztg. 1896, **21**, (18), 563; abst. J. S. C. I. 1896, **15**, 370; Ber. Österr. Ges. z. Förder d. Chem. Ind. 1894, **16**, 119; abst. J. S. C. I. 1895, **14**, 72. H. Wrede, Papierfabr. 1909, **7**, (Fest und Auslandsh), 43–46; abst. J. S. C. I. 1909, **28**, 811; Wochenbl. Papierfabr. 1911, **42**, 582–584; abst. J. S. C. I. 1911, **30**, 278. A. Wright, E. P. 12903, 1887; abst. J. S. C. I. 1888, **7**, 640. C. Wurster, Ber. 1887, **20**, 808–810; abst. J. S. C. I. 1887, **6**, 565; Papier Ztg. 1903, **28**, (46), 1608–1609; abst. J. S. C. I. 1903, **22**, 824; abst. J. S. C. I. 1903, **22**, 817; U. S. P. 690506, 1902; abst. J. S. C. I. 1902, **21**, 271; U. S. P. 690505, 1902; abst. J. S. C. I. 1902, **21**, 271. T. Young and J. Pettigrew, Jr., E. P. 14735 and 14998, 1884; abst. J. S. C. I. 1885, **4**, 364. D. R. P. 280476, 1914; abst. J. S. C. I. 1915, **34**, 488. F. Zacharias, Papierfabrikant, 1912, **10**, 65–70, 98–99, 132–135, 168–170, 195–198, 222–226, 253–257, 274–277, 301–303, 333–337, 362–365, 391–394, 423–426, 452–455, 502–504; D. R. P. 117380, 1900; abst. J. S. C. I. 1912, **31**, 582. C. Ziegelmeyer, Papier Ztg. 1918, **42**, 1855–1856; Zts. ang. Chem. 1918, **31**, 174–175; abst. J. S. C. I. 1918, **37**, 408-A. A. Zimmermann, J. Roy. Soc. Arts, 1912, **61**, 69–81; abst. J. S. C. I. 1912, **31**, 1197; E. P. 3963, 8359 and 13746, 1913; abst. J. S. C. I. 1914, **33**, 348. O. Zimmermann and G. Hagemann, E. P. 10326, 1894; abst. J. S. C I. 1895, **14**, 676. F. Zweigler, Papierfabrikant, 1912, **10**, 1364–65; abst. J. S. C. I. 1913, **32**, 18. Anon., Pap. Ztg. 1916, **16**, 1446, 1447. F. Abraham, Gerberei-Technik, 1913, No. 11, 12; Collegium, 1913, 11, 599; J. S. C. I. 1913, **32**, 1079. H. Achenbach, D. R. P. 286601, 1914; Add. to D. R. P. 252412, 1911; Nor. P. 23689, 1913; abst. C. A. 1916, **10**, 2148; Papir J. 1913, **1**, 30. F. Ahrens, Zts. ang. Chem. 1895, **8**, 41; abst. J. S. C. I. 1895, **14**, 503. Chem. Zts. 1903, **2**, 743; abst. Chem. Centr. 1903, **74**, II, 812. Pap. Ztg. 1905, **30**, I, 1539; Chem. Zentr. 1905, **76**, I, 700; Chem. Zts. 1905, **4**, 40; J. S. C. I. 1905, **24**, 343. Aktiebolaget Ethyl, Sweden, F. P. 446717, 446718, 1912; abst. Chem. Ztg. Rep. 1913, **37**, 116; J. S. C. I. 1913, **32**, 133, 377; C. A. 1913, **7**, 1972, 2115. Nor. P. 24757, 1914; 27613, 1917; abst. Papir J. 1914, **2**, 263; C. A. 1917, **11**, 1903; Pulp Paper Mag. Can. 1917, **15**, 765, 788. Aktiebolaget Ethyl and G. Ekstrom, Aust. P. Anm. 940, 1913; Swed. P. 35232, 1912. Aktieselskabet Sulfitspirit, Hol. P. 1763, 1917; Nor. P. 25927, 1915; abst. Papir J. 1915, **3**, 190; C. A. 1917, **11**, 1300; Pulp and Paper Mag. Can. 1917, **15**, 541. M. Albersheim, D. R. P. Anm. K. Albert and L. Behrend, D. R. P. 250275, 1911; abst. Chem. Zentr. 1912, **83**, II, 779. H. Alt, Farber Ztg. 1899, **10**, 303; abst. Wag. Jahr. 1899, **45**, 972. W. Appelius, J. Amer. Leather Chem. Assoc. 1915, **10**, 202; Ledertechn. Rundschau, 1915, **7**, 17; J. S. C. I. 1915, **34**, 501. W. Appelius and R. Schmidt, Ledertechn. Rundschau, 1914, **6**, 225; Zts. ang. Chem. 1914, **27**, 691; Collegium, 1914, 706; J. Amer. Leather Chem. Assoc. 1914, **9**, 64; J. S. C. I. 1915, **34**, 189. O. Arlt, D. R. P. 128213, 1898; abst. Chem. Zentr. 1902, **73**, I, 446; Chem. Ztg. 1901, **26**, 229; Pap. Fabr. 1905, **3**, 785; J. Auerbach, Chem. Ztg. 1913, **37**, 906. D. Aufhauser, Zts. ang. Chem. 1912, **25**, 74. B. Bache-Wiig, D. R. P. 129326, 1901; abst. Chem. Centr. 1902, **73**, I, 740. G. Badermann, Zts. ang. Chem. 1910, **23**, 1216; J. S. C. I. 1910, **29**, 874. Badische Anilin & Soda Fabrik, D. R. P. 222191, 1900; 265536, 1912; abst. Chem. Ztg. Rep. 1910, **34**, 271; Wochenbl. Papfabr. 1910, **41**, 2612; Chem. Zentr. 1910, **81**, I, 1998. L. Bakeland, U. S. P. 1057319, 1913;

coarse filaments made into rovings and nitrated as such, in much

---

abst. J. S. C. I. 1913, **32,** 428; C. A. 1913, **7,** 1796; Paper Trade J. 1913, **57,** No. 20, 46. G. Banthier, J. Gasbel. 1914, **57,** 32, 55; J. S. C. I. 1914, **33,** 129; C. A. 1914, **8,** 1344. G. Bantlin, J. Gasbel. 1914, **57,** 32; Chem. Zentr. 1914, **85,** I, 923; C. A. 1914, **8,** 1344. K. Barth, Pap. Ztg. 1890, **15,** 667. J. Bates, Pulp, Paper Mag. Can. 1917, **15,** 553. H. Becker and F. Gross, Ledertechn. Rundschau, 1914, **6,** Oct. 22; abst. Collegium, 1915, 106; J. S. C. I. 1915, **34,** 501. H. Bennett, Shoe and Leather Rep. 1912, **104,** 31; C. A. 1912, **6,** 1383. E. Bergerhoff, D. R. P. 160151, 1903; abst. Bied. Tech. Chem. Jahr. 1904, 558; Chem. Zentr. 1905, **76,** I, 1576. H. Bergstrom, Jernkontorets Annaler, 1909, 691; Papier Fabr. 1909, **7,** 506, 607; **8,** 970; J. S. C. I. 1909, **28,** 1162; Zts. ang. Chem. 1910, **23,** 1823. D. R. P. 290680, 1914; Nor. P. 27849, 1914; abst. C. A. 1917, **11,** 888; Pulp, Paper Mag. Can. 1917, **15,** 809. Pap. Fabr. 1912, **10,** 359; J. S. C. I. 1912, **31,** 381; C. A. 1912, **6,** 2528. Pap. Fabr. 1914, **12,** 1040; abst. Zts. ang. Chem. 1915, **28,** 47; J. S. C. I. 1915, **34,** 487; C. A. 1915, **9,** 149; Chem. Trade J. 1915, **57,** 208; Papier J. 1914, **2,** 389. H. Bergstrom and B. Lindquist, Swed. P. 33333, 1910; abst. C. A. 1913, **7,** 1288. J. Beveridge, J. S. C. I. 1916, **35,** 563; Paper, 1916, **18,** No. 16, 17; C. A. 1916, **10,** 2799. D. Bibb, U. S. P. 1158364, 1158365, 1158366, 1915; Nor. P. 27881, 1917; abst. J. S. C. I. 1915, **34,** 1119; Pap. Fabr. 1917, **5,** No. 13, 111. B. Blackman, U. S. P. 369530, 369634, 369836, 530635, 1895; abst. Pap. Ztg. 1895, **20,** I, 1376; II, 2152. D. Hanson, U. S. P. 1330632, 1920. D. R. P. 266122, 1912; abst. J. S. C. I. 1913, **32,** 1104; C. A. 1914, **8,** 822. K. Bloesch, Russ. Privilegium, 558, 1898; abst. Chem. Ztg. 1898, **23,** 320. J. Briggs, Chem. World, 1914, **2,** 346; C. A. 1914, **8,** 1204; Paper Makers Brit. Trade J. Ann. No. 1913–1914, 66; Paper 1913, **13,** No. 11, 21. E. Bruck, Chem. Ztg. 1892, **95,** 1782; abst. J. S. C. I. 1893, **12,** 460. L. Brunet, F. P. 459069, 1912; abst. C. A. 1914, **8,** 2805; J. S. C. I. 1913, **32,** 1153. O. Bryant, Pulp. Paper Mag. Can. 1915, **13,** 139; Paper, 1915, **15,** No. 26, 15. H. Bucherer, Pap. Ztg. 1905, **30,** I, 1350; Zts. ang. Chem. 1904, **17,** 31. W. Buddens, Pap. Ztg. 1891, **16,** 1813. J. Buisson, F. P. 442809, 1912; abst. Chem. Ztg. Rep. 1912, **36,** 69; J. S. C. I. 1912, **31,** 1120. F. P. 449350, 1912. F. Byrom, E. P. 24196, 1914; abst. J. S. C. I. 1915, **34,** 1063; C. A. 1916, **10,** 1610. T. Carlson, Pap. Fabr. 1909, **7,** 587. Pap. Ztg. 1910, **35,** II, 2117. Carpenter and Schulze, D. R. P. 78306, 1894; Add. to D. R. P. 71942; abst. Ber. 1896, **28,** 260. Chemische Fabrik Floersheim, D. R. P. 247119, 1910. Chemische Fabrik Grünan, Landshoff and Meyer, D. R. P. 48269, 1888; abst. Pap. Ztg. 1889, **14,** 2310. Chem. Fabrik K. Kopper and F. Kammer, D. R. P. 114401, 1899; abst. Chem. Zentr. 1900, **71,** II, 1046. Chemische Industrie und Handels Ges. D. R. P. 248055, 1910; abst. J. S. C. I. 1912, **31,** 999. P. Claes, Belg. P. 244151, 1912. A. Claflin, J. Amer. Leather Chem. Assoc. 1912, **7,** 154; abst. Zts. ang. Chem. 1912, **25,** 1932; C. A. 1912, **6,** 1383. A. Classen, D. R. P. 161644, 1903; abst. Chem. Zentr. 1905, **76,** II, 560. M. Coughlin, U. S. P. 1103267, 1914; 1217157, 1917; abst. J. S. C. I. 1914, **33,** 931; 1917, **36,** 512. M. Coughlin and C. Sweet, U. S. P. 1114119, 1114120, 1914; abst. C. A. 1914, **8,** 3858; J. S. C. I. 1914, **33,** 1152, 1153; Paper, 1914, **15,** No. 7, 24, 32. C. Cross and E. Bevan, E. P. 1548, 1883; abst. J. S. C. I. 1883, **2,** 541. A. Cushman, J. S. C. I. 1911, **30,** 211. J. DeCew, U. S. P. 1010122, 1911; 1155708, 1915; Nor. P. 26293, 1915; abst. J. S. C. I. 1912, **31,** 29; 1915, **34,** 1244; Papir J. 1915, **3,** 262; Paper Maker Brit. Trade J. 1915, **49,** 332. J. DeCew, U. S. P. 1203856, 1916; abst. J. S. C. I. 1916, **35,** 1257; C. A. 1917, **11,** 100; Paper Makers Monthly J. 1916, **54,** 212. F. Detsinyi, Aust. P. 10987, 1898; abst. Pap. Ztg. 1898, **23,** I, 950. Deutsche Saduyn Gesellschaft, Wochenbl. Papfarb. 1910, **41,** 3847. B. Diamond, U. S. P. 938128, 940394; E. P. 5206, 1909; D. R. P. 216798, 222193, 1909; abst. J. S. C. I. 1909, **28,** 1239; Zts. ang. Chem. 1910, **23,** 1390; Chem. Ztg. Rep.

the manner that Memphis Star and other comparatively long fiber

1909, **33,** 607, 624; Wag. Jahr. 1909, **55,** I, 492. W. Dickerson, E. P. 7438, 1910; abst. J. S. C. I. 1911, **30,** 438. U. S. P. 1043303, 1912; abst. Paper Trade J. 1913, **57,** No. 2, 42; Wochenbl. Papfabr. 1912, **44,** 4796; J. S. C. I. 1912, **31,** 1140. J. Amer. Leather Chem. Assoc. 1914, **9,** 489; J. S. C. I. 1914, **33,** 1163. U. S. P. 1059716, 1913; abst. J. S. C. I. 1913, **32,** 531; C. A. 1913, **7,** 2115. Paper, 1917, **19,** No. 20, 19; No. 21, 17. R. Dieckmann and E. Hagglund, Chem. Ztg. 1916, **40,** 581; C. A. 1917, **11,** 1544. L. Dorenfeldt, E. P. 11974, 1898; D. R. P. 122489, 1898; Aust. Privilegium, 4602, 1898; Pap. Ztg. 1898, **23,** 652; 1900, **26,** I, 2602; Chem. Centr. 1900, **71,** II, 248; J. S. C. I. 1898, **17,** 788; 1899, **18,** 702. D. R. P. 113435, 1898; 129227, Aust. Privilegium, 3807, 1898; abst. Pap. Ztg. 1900, **25,** II, 2916; Chem. Centr. 1900, **71,** II, 702; 1902, **73,** I, 686. Zts. ang. Chem. 1901, **14,** 82. V. Drewsen, E. P. 2629, 1892; abst. J. S. C. I. 1893, **12,** 461. Durr & Co. D. R. P. 71942, 1893; abst. Ber. 1894, **27,** 220. W. Eitner, Gerber, 1911, **37,** 227, 241, 255; 1913, **39,** 43, 57; abst. J. S. C. I. 1911, **30,** 1269; 1913, **32,** 229. C. Ekmann, E. P. 20036, 1893; D. R. P. 81643, 1893; abst. Ber. 1896, **28,** 711; Pap. Ztg. 1896, **21,** I, 2218, 2609, 3247; J. S. C. I. 1894, **13,** 1085; 1896, **15,** 735; Aust. Privilegium, 569, 1894. C. Eckman, D. R. P. 109951, 1899; E. P. 189, 1899; Aust. P. 3229, 1899; abst. Pap. Ztg. 1900, **25,** 797; J. S. C. I. 1899, **18,** 1150. G. Ekstrom, Svensk. Kem. Tid. 1909, No. 7; Pap. Ztg. 1910, **35,** II, 2519. Pap. Fabr. 1910, **8,** 582; abst. J. S. C. I. 1910, **29,** 810; Chem. Ztg. 1910, **34,** 223; Wochenbl. Pap. Fabr. 1910, **41,** 638; E. P. 6741, 1910; Can. P. 132717, 1911; abst. J. S. C. I. 1911, **30,** 504. Swed. P. 34623, 1912; abst. C. A. 1914, **8,** 1669. Can. P. 142290, 1912; abst. C. A. 1914, **8,** 2251; Paper, 1914, **14,** No. 22, 20. U. S. P. 1042332, 1912; Can. P. 142288, 1912; abst. J. S. C. I. 1912, **31,** 1075; Papir, 1912, **10,** No. 9, 16. U. S. P. 1046160, 1912; Can. P. 142289, 1912; abst. J. S. C. I. 1913, **32,** 103; C. A. 1913, **7,** 677; Paper, 1912, **10,** No. 9, 16. U. S. P. 1050723, 1913; Swed. P. 34624, 1912; Can. P. 142287, 1912; abst. J. S. C. I. 1913, **32,** 192; C. A. 1913, **7,** 889; 1914, **8,** 1669. Swed. P. 33876; abst. Chem. Ztg. 1913, **37,** No. 31, 32. Svensk. Pap. Tid. 1913, 2258; Papir J. 1914, 298; Pap. Ztg. 1910, **35,** 3244; 1913, **38,** 2258. Pap. Ztg. 1914, **39,** 269; Wochenbl. Papfabr. 1914, **45,** 825. U. S. P. 1098561, 1098562, 1914; Can. P. 142285, 142286, 1912; abst. J. S. C. I. 1914, **33,** 785; C. A. 1914, **8,** 2803. Swed. P. 35706, 1912; abst. Pap. Fabr. 1914, **12,** 727. Pulp, Paper Mag. Can. 1915, **13,** 68; C. A. 1915, **9,** 1114. Paper J. 1914, **2,** 298. U. S. P. 1139507, 1915; Can. P. 142542, 142543, 1912; abst. J. S. C. I. 1915, **34,** 729; C. A. 1914, **8,** 2251, 2803; 1915, **9,** 1825. U. S. P. 1087356, 1914; abst. Chem. Ztg. 1914, **38,** 25; J. S. C. I. 1914, **33,** 349; C. A. 1914, **8,** 1346. M. Elb, D. R. P. 166947, 1905; Aust. P. 23046, 1905; abst. Pap. Ztg. 1906, **31,** I, 215; Chem. Centr. 1906, **77,** I, 801. D. R. P. 173686, 1905; abst. Pap. Ztg. 1906, **31,** II, 3180; Chem. Centr. 1906, **77,** II, 924. C. Ellis, U. S. P. 1042538, 1912; abst. J. S. C. I. 1912, **31,** 1120. U. S. P. 1057416, 1912; abst. J. S. C. I. 1913, **32,** 482; C. A. 1913, **7,** 1806; Pulp, Paper Mag. Can. 1912, **10,** 372. U. S. P. 877414, 1908; abst. Chem. Ztg. Rep. 1908, **32,** 111; J. S. C. I. 1908, **27,** 177. U. S. P. 1223158, 1917; abst. J. S. C. I. 1917, **36,** 593; C. A. 1917, **11,** 1903; Pulp, Paper Mag. Can. 1917, **15,** 741. U. S. P. 1068084, 1913; abst. J. S. C. I. 1913, **32,** 829. U. S. P. 1119500, 1914; abst. J. S. C. I. 1915, **34,** 82. Erste Oesterreichische Sodafabrik, Aust. P. 2336, 1889. Farbenfabriken vorm F. Bayer & Co., D. R. P. 264920, 265167, 1912. Farbwerke Friedrichsfeld, P. Remy, D. R. P. 90798, 1896; abst. Pap. Ztg. 1897, **22,** I, 426; J. S. C. I. 1897, **16,** 630. Feldmühle Papier und Zellstoffwerke, D. R. P. 307087, 307663, 1918; abst. J. S. C. I. 1920, **39,** 16-A. S. Ferenczi, Pap. Ztg. 1897, **22,** 3575, 3647, 3679; abst. J. S. C. I. 1898, **17,** 264. J. Landw. **60,** 183; abst. Zts. ang. Chem. 1912, **25,** 2088. A. Fest, U. S. P. 1218638, 1917; C. A. 1917, **11,** 1545; Pulp, Paper Mag. Can.

cottons are hand or pot nitrated at the present day for the prep-

1917, **15,** 677; Paper, 1917, **20,** No. 11, 22. F. Fittica, Pap. Ztg. 1902, **27,** II, 3144. G. Forrester, Paper, 1912, **6,** No. 11, 15. H. Fosse, Ber. Pharm. Ges. 1915, **25,** 303; abst. J. S. C. I. 1915, **34,** 1261. A. Foster, U. S. P. 1320043, 1919; abst. J. S. C. I. 1919, **38,** 959-A. G. Foth, Zts. Spiritusind, 1910, 589; abst. Chem. Ztg. 1911, **35,** 35; C. A. 1911, **5,** 1970. Chem. Ztg. 1913, **37,** 1221. A. Frank, E. P. 13286, 1886; abst. J. S. C. I. 1887, **6,** 735. Aust. P. 646, 1887. Pap. Ztg. 1904, **29,** II, 2465; 1906, **31,** II, 3322. D. R. P. 40308, 1886; abst. Ber. 1887, **20** 667; Pap. Ztg. 1887, **12,** 1170. Pap. Ztg. 1887, **12,** 1765, 1782, 1832; 1888, **13,** 531; abst. Dingl. Poly. 1888, **268,** 485; 1890, **276,** 58. Pap. Ztg. 1889, **14,** 1488. Pap. Ztg. 1910, **35,** I, 145. Pap. Ztg. 1889, **14,** 383, 1488, 1556. Das Papier, 1907, **2,** 134. Wochbl. Papierfabr. 1907, **38,** 3199. A. Frank and E. Lehmann, Pap. Ztg. 1904, **29,** II, 3368; Wochenbl. Papfabr. 1904, **35,** 3338. W. Freeman, U. S. P. 1175422, 1175423, 1175424, 1175425, 1175426, 1916; abst. C. A. 1916, **10,** 1434; J. S. C. I. 1916, **35,** 533. A. Gansser, Collegium, 1909, 360; 1912, 482; 1914, 324; Zts. ang. Chem. 1913, **26,** 528; Chem. Ztg. Rep. 1913, **37,** 442; J. S. C. I. 1914, **33,** 654; C. A. 1915, **9,** 535. A. Gawalowski, Pap. Ztg. 1899, **24,** 3112; E. Gewerkschaft, D. R. P. 200210, 1907; abst. Chem. Ztg. 1908, **32,** 478; Pap. Ztg. 1908, **33,** II, 2014. Swed. P. 23464, 1906; abst. Chem. Ztg. Rep. 1908, **32,** 82. D. R. P. 246289, 1908. D. R. P. 252439, 1908; abst. Zts. ang. Chem. 1912, **25,** 2359; C. A. 1913, **7,** 416. G. Gianoli, U. S. P. 1063428, 1913, abst. J. S. C. I. 1913, **32,** 760. E. Goldschmidt, D. R. P. 97935, 1897; abst. Chem. Centr. 1898, **69,** II, 616; Pap. Ztg. 1898, **23,** 2664. Chem. Ztg. 1898, **22,** 374; J. S. C. I. 1898, **17,** 790. L. Gottstein, Wochenbl. Papfabr. 1905, **36,** I, 1390, 1616, 1779; abst. Pap. Ztg. 1907, **26,** I, 828; abst. J. S. C. I. 1901, **20,** 495. Chem. Ztg. 1914, **38,** 804. Pap. Ztg. 1889, **14,** 1556. Pap. Ztg. 1906, **31,** 952; abst. Zts. ang. Chem. 1906, **19,** 293. Wochenbl. Papierfabr. 1912, **43,** 4329. Chem. Ztg. 1914, **38,** 804. O. Goy, Zts. ang. Chem. 1913, **23,** 602; Landw. Vers. Sta. 1913, **82,** 1; C. A. 1913, **7,** 4023. B. Graetz, D. R. P. 211479, 1912; Chem. Ztg. Rep. 1914, **38,** 175; J. S. C. I. 1914, **33,** 471. D. R. P. 280455, 1913; abst. J. S. C. I. 1915, **34,** 540. Swiss P. 73107, 1916; Dan. P. 21889, 1917; abst. C. A. 1917, **11,** 100; Pulp, Paper Mag. Can. 1917, **15,** 741. P. Grempe, Wochenbl. Papfabr. 1912, **43,** 3417. L. Griffin, D. R. P. 69874, 1892; abst. Ber. 1893, **26,** 905. Paper Trade J. Conv. No. 1911; Paper Maker Brit. Trade J. 1911, **17,** 55. Pulp, Paper Mag. Can. 1906, **4,** 75. F. Gross, D. R. P. Anm. 38003, 1912. U. S. P. 1154762, 1915; abst. J. S. C. I. 1915, **34,** 1139, 1155; C. A. 1915, **9,** 3378. G. Grosser, Technikum, 1912, **20,** 156; Chem. Ztg. 1913, **37,** 442; Collegium, 1912, 510, 557; 1913, 479. O. Grothe, U. S. P. 1087911, 1914; abst. C. A. 1914, **8,** 1357; J. S. C. I. 1914, **33,** 349. Paper Trade J. 1915, **60,** 52. Nor. P. 25315, 1915; abst. Papir J. 1915, **3,** 37. W. Gunther, D. R. P. 255853, 1910; abst. J. S. C. I. 1913, **32,** 284; C. A. 1913, **7,** 1869. W. Gunther, F. P. 457159, 1913; abst. C. A. 1914, **8,** 2018. W. Haage, D. R. P. 228721, 1908; abst. Chem. Zentr. 1911, **82,** II, 1789; Pap. Ztg. 1911, **36,** 67; C. A. 1911, **5,** 2177. A. Haeffner, U. S. P. 1231153, 1917; abst. Paper, 1917, **20,** No. 21, 23; Paper Making, 1917, **36,** 238; Pulp, Paper Mag. Can. 1917, **15,** 1031; Paper Makers Monthly J. 1917, **55,** 277. E. Hagglund, Chem. Ztg. 1916, **40,** 433; C. A. 1915, **9,** 2925; 1916, **10,** 2636; J. S. C. I. 1916, **35,** 832. Pulp, Paper Mag. Can. 1917, **15,** 1125, 1157, 1185; Paper, 1917, **21,** 11; No. 17, 16; No. 18, 13; No. 19, 11, 20; No. 20, 15. Pap. Fabr. 1916, **14,** 353. A. Harpf, Dingl. Poly. 1892, **286,** 84, 112. H. Harpf, Zts. ang. Chem. 1898, **11,** 875, 925, 1169; Chem. Centr. 1899, **70,** 313. W. Harrocks, and J. Tullis, E. P. 18332, 1914; abst. J. S. C. I. 1915, **34,** 1063. Hartmann, Pap. Ztg. 1895, **20,** 822, 952, 1084; 1896, **21,** 764; 1899, **24,** 1667. A. Harvey, Leather World, 1917, **9,** 73. A. Haussner, Dingl. Poly. 1890, **275,** 577, **276,** 49; **277,** 118, 174, 211; Jahr.

aration of high class water-white pyroxylin lacquers for the protec-

Chem. 1890, **43,** 2876. J. Hedalen, Pulp, Paper Mag. Can. 1916, **14,** 176; Paper, 1916, **18,** No. 17, 15; C. A. 1916, **10,** 2403. M. Hedden, U. S. P. 1130817, 1915; abst. J. S. C. I. 1915, **34,** 419; C. A. 1915, **9,** 1115. E. Hendrick, Met. Chem. Eng. 1918, **18,** 360; abst. Paper Makers Monthly J. 1918, **56,** 136; Paper, **22,** No. 4, 13. Hoesch & Co., E. P. 21994, 1911; F. P. 434943, 1911; Belg. P. 239604; Hung. P. Appl. 4348, 1911; abst. J. S. C. I. 1912, **31,** 351, 696. H. Hofer, Allgem. Fischerei Ztg. 1908, **31,** 71. Allgem. Fischerei Ztg. 1915, No. 20, 21; Pap. Ztg. 1916, **41,** 1; C. A. 1916, **10,** 1432. C. Hofmann, Pap. Ztg. 1896, **21,** II, 2483. M. Honig, E. P. 18265, 1896; abst. J. S. C. I. 1896, **15,** 819. Russ. Privilegium, 953, 1898; abst. Chem. Ztg. 1899, **23,** 319. U. S. P. 727798, 1903; D. R. P. 132224, 1901; Aust. P. 7325, 1901; Pap. Ztg. 1902, **27,** II, 2162; Chem. Centr. 1902, **73,** II, 174; J. S. C. I. 1903, **22,** 753. D. R. P. 152236; Aust. P. 12970, 1902; abst. Pap. Ztg. 1903, **29,** II, 2226; Wag. Jahr. 1904, **50,** II, 514. Aust. P. 31862, 1906; Add. to Aust. P. 7325. F. P. 413849, 1910; Aust. P. Appl. 3325, 1910, Hung. P. Appl. 3806, 1910; Chem. Ztg. Rep. 1910, **34,** 251; Zts. ang. Chem. 1910, **23,** 499; J. S. C. I. 1910, **29,** 1121. E. P. 7066, 1910; abst. C. A. 1911, **5,** 2989. D. R. P. Anm. H. 56968, 1912; Aust. Anm. A. 1511; Add. to Aust. P. 43742. U. S. P. 1080970, 1913; abst. C. A. 1914, **8,** 591. J. S. C. I. 1912; **31,** 768; Chem. Ztg. 1912, **36,** 880; C. A. 1912, **6,** 3517; Paper, 1912, **9,** No. 1, 29; Paper-Maker, Brit. Trade J. 1915, 497. W. Hoskins, U. S. P. 1226333, 1917; abst. C. A. 1917, **11,** 2153; Pulp, Paper Mag. Can. 1917, **15,** 741. W. Hough, E. P. 19116, 1909; abst. C. A. 1911, **5,** 1839. W. Hough, U. S. P. 931608; abst. Pap. Ztg. 1909, 2787; Pulp, Paper Mag. Can. 1910, **8,** 48. H. Hurt, U. S. P. 1075916, 1913; 1147245, 1915; abst. C. A. 1913, **7,** 4095; 1915, **9,** 2465. J. S. C. I. 1913, **32,** 1079; 1915, **34,** 915; Paper Trade J. 1913, **58,** 44. E. Hutchins, Paper, 1913, **13,** No. 3, 17; No. 4, 15; No. 5, 17; C. A. 1913, **7,** 2855. International Association of Leather Trade Chemists, Enke, Stuttgart, 1910, **1,** 689; 1911, **3,** 15. A. Jabs, D. R. P. 287015, 1912; abst. J. S. C. I. 1916, **35,** 103. F. Jedlica, Collegium, 1913, 489. A. Jernberg, U. S. P. 1221058, 1917; abst. C. A. 1917, **11,** 1750; J. S. C. I. 1917, **36,** 561; Pulp, Paper Mag. Can. 1917, **15,** 719. F. Jürgensen, F. Niesz and G. Gümbel, D. R. P. 73718, 1892; abst. Ber. 1894, **27,** 445. A. Katz, D. R. P. 149461, 1903; abst. Pap. Ztg. 1904, **29,** I, 800; Wag. Jahr. 1904, **50,** II, 533, Kausch, Kunst. 1913, **3,** 112, 127. H. Kayser, Wochenbl. Papfabr. 1908, **39,** 2201. Pap. Ztg. 1910, **35,** 768. D. Kempe, Aust. Privilegium 3962, 1897; Swed. P. 8422, 1897; abst. Chem. Ztg. 1898, **22,** 26. F. Kennard, U. S. P. 1138118, 1915; abst. C. A. 1915, **9,** 1691; J. S. C. I. 1915, **34,** 656; J. Ind. Eng. Chem. 1915, **7,** 1008. L. Kern, D. R. P. 278492, 1914; abst. Pap. Ztg. 1914, **39,** 2500; J. S. C. I. 1915, **34,** 240. Wochenbl. Papfabr. 1915, **46,** 278; C. A. 1915, **9,** 1086. W. Kerp and P. Wohler, Pap. Ztg. 1913, **38,** 3063; Arbeit. Kais. Gesundh. **32,** 120. G. Kerschaw, Pulp, Paper Mag. Can. 1915, **13,** 111. Z. Kertesq, Chem. Ztg. 1916, **40,** 945; abst. C. A. 1917, **12,** 1040; Paper Maker and Brit. Trade J. 1917, **52,** 36; Pulp, Paper Mag. Can. 1917, **15,** 236, 306; Paper Makers Monthly J. 1917, **55,** 49; Paper, 1917, **19,** No. 17, 15. P. Kestner, D. R. P. Anm. 46236, 1910. W. Kiby, Chem. Ztg. 1910, **34,** 1077, 1091; C. A. 1911, **5,** 785; J. S. C. I. 1910, **29,** 1265. Chem. Ztg. 1915, **39,** 212, 261, 284, 350; abst. C. A. 1915, **9,** 2311; 1916, **10,** 116; Paper, 1915, **17,** No. 15, 12. A. Kielmeyer, Farber Ztg. 1899, 34; abst. Wag. Jahr. 1899, **45,** 972. E. Kirchner, Das Papier, **2,** pt. B, C, 122, 126. I. Kitsee, U. S. P. 942207, 1909; abst. J. S. C. I. 1910, **29,** 83; C. A. 1910, **4,** 668. A. Kjaer & Co., Nor. P. 27637, 1917; abst. C. A. 1917, **11,** 1902; Pulp and Paper Mag. Can. 1917, **15,** 741. P. Klason, Pap. Ztg. 1909, **34,** I, 1315; Pap. Fabr. 1909, **7,** 445; Zts. ang. Chem. 1909, **22,** 1423. Wochenbl. Papfabr. 1909, **40,** 2668; Pap. Fabr. 1909, **7,** 26, 671, 701, 795; J. S. C. I. 1909, **28,** 1000; Pap. Ztg. 1910, **35,** 2116; Pulp, Paper Mag. Can.

tion of silverware. For the manufacture of pyroxylin artificial

1910, **8**, 185; Paper, 1911, **3**, No. 2, p. Pap. Ztg. 1910, **35**, 375, 451, 731. Pap. Fabr. 1916, **14**, 657, 739. Svensk Pap. Tid. 1916, **19**, 115; 1917, **20**, 176. Svensk Pap. Tid. 1917, **20**, 176. P. Klason and Segerfeld, Svensk. Kem. Tidskrift. Paper, 1914, **13**, No. 18, 18; C. A. 1914, **8**, 1345. A. Klein, Pap. Ztg. 1909, **34**, I, 227; Wochenbl. Papfabr. 1909, **40**, 240. Papfabr. 1914, **12**, 601, 639; abst. J. S. C. I. 1914, **33**, 1201; Paper, 1914, **14**, No. 22, 15; No. 23, 16; No. 24, 22; No. 25, 17. O. Knight, U. S. P. 1143714, 1915; abst. J. S. C. I. 1915, **34**, 830; Paper Trade J. 1915, **61**, No. 3, 50; Paper, 1915, **17**, No. 2, 18. T. Knoesel, Pap. Ztg. 1898, **23**, I, 1503. Wochenbl. Papfabr. 1908, **39**, 3276; 1909, **40**, 4049; C. A. 1909, **3**, 484, 1083. D. Landw. Presse, 1902, No. 4; Chem. Ztg. 1902, **26**, 229; Chem. Zentr. 1902, **73**, I, 955; Pap. Ztg. 1903, **28**, I, 288; J. S. C. I. 1902, **21**, 489. Pap. Fabr. 1904, **2**, 759; 1905, **3**, 1914. D. Landw. Presse, 1902, No. 4, 63; 1905, No. 4, 13; Chem. Ztg. 1902, **26**, 329; 1903, **27**, 21; 1904, **28**, 38; Chem. Zentr. 1902, **73**, I, 955; Pap. Ztg. 1903, **28**, I, 288; 1905, **30**, I, 1539; 1904, **29**, II, 3367; Wochenbl. Papfabr. 1905, **33**; Pap. Fabr. 1904, **2**, 759; 1905, **3**, 1714; Chem. Zts. 1905, 40; Zts. ang. Chem. 1904, **17**, No. 47; Wochenbl. Papfabr. 1908, **38**, II, 2542; F. P. 423562, 1910; abst. J. S. C. I. 1911, **30**, 638. Pap. Ztg. 1911, **36**, 2193. Holzstoff Ztg. 1913, **20**, 775. Zts. Sauerstoff Stickstoff Ind. 1912, **4**, 65. A. Knopflmocher, E. P. 102608, 1916; abst. Paper Makers Monthly J. 1917, **55**, 259; J. S. C. I. 1917, **36**, 589. R. Kolkwitz, Wochenbl. Papierfabr. 1907, **38**, 1998, 2289. Ber. Botan. Ges. 1912, **30**, 9. R. Kolkwitz and Pritzkow, Chem. Zentr. 1908, **79**, II, 2048; Wochenbl. Papfabr. 1908, **39**, 332. Mitt. Prufungsamt. Wasser u Abwasser. 1909, **10**, 173, 1116; abst. C. A. 1909, **3**, 1661, 1662. J. Konig, Zts. Nahr. Genussm. 1913, **26**, 273; Chem. Zentr. 1913, **84**, II, 1700. U. S. P 1128154, 1915; F. P. 469768, 1914; D. R. P. 284715, 1914; abst. C. A. 1916, **10**, 76; J. S. C. I. 1915, **34**, 47, 299; Paper, 1914, **15**, No. 22, 17. Nor. P. 26029, 1915; Swed. P. 40438, 1916; abst. C. A. 1916, **10**, 2045; Papir J. 1915, **3**, 203. Zts. Nahr. Genussm. 1916, **31**, 171; abst. Papir J. 1916, **4**, 187; Zts. ang. Chem. 1916, **29**, 379; C. A. 1916, **10**, 3114; J. S. C. I. 1916, **35**, 960. Zts. ang. Chem. 1906, **19**, 750. Chem. Ztg. 1887, **11**, 1111. Pap. Ztg. 1887, **12**, 770. Zts. ang. Chem. 1906, **19**, 750. T. Korndorff, D. R. P. 32696; 1886; abst. Pap. Ztg. 1886, **11**, 1419. G. Krause, U. S. P. 1213887, 1917, abst. J. S. C. I. 1917, **36**, 329. H. Krause, Chem. Ind. 1906, **29**, 217; Pap. Ztg. 1907, **32**, I, 1100; J. S. C. I. 1906, **25**, 493. W. Krep and P. Wohler, Arbeit. Kais. Gesundh. 1909, **23**, 120; Chem. Zentr. 1909, **62**, II, 710; Pap. Fabr. 1909, **7**, 45, 1135; Pap. Ztg. 1909, **34**, 3286; 1910, **35**, 1932; J. S. C. I. 1909, **28**, 1001; C. A. 1910, **4**, 443. E. Kressel, U. S. P. 1225825, 1917; abst. C. A. 1917, **11**, 2255; J. S. C. I. 1917, **36**, 730. F. Kruger, Mon. Sci. 1905, **63**, 801; Farben Ztg. 1906, **11**, 237. A. Kuhn, Wochenbl. Papfabr. 1916, **47**, 2139, 2179, 2233, 2270; abst. J. S. C. I. 1917, **36**, 639; Chem. Ztg. Rep. 1917, **41**, 148; Paper, 1917, **20**, No. 24, 13; Pulp Paper Mag. Can. 1917, **15**, 857, 1009. R. Kuhn, Pap. Ztg. 1895, **20**, 1083, 1351, 1445. A. Kumpfmiller, D. R. P. 203648, 1906; abst. C. A. 1909, **3**, 714; J. S. C. I. 1908, **27**, 1174. Aust P. 40657, 1906. D. R. P. 183415, 1905; abst. Wag. Jahr. 1907, **53**, II, 503; Chem. Zentr. 1907, **78**, II, 109; Wochenbl. Papfabr. 1907, **38**, 1402; Pap. Ztg. 1907, **32**, I, 2046; Chem. Ztg. Rep. 1907, **31**, 243. D. R. P. 203648, 1906; abst. Chem. Zentr. 1908, **79**, II, 1834; Pap. Ztg. 1908, **33**, II, 3564; Chem. Ztg. 1908, **32**, 1036; Wochenbl. Papfabr. 1909, **40**, 260; J. S. C. I. 1908, **27**, 1174; C. A. 1909, **3**, 714. Aust. P. 40657, 1906. D. R. P. 194872, 1906; abst. Chem. Zentr. 1908, **79**, I, 118; Pap. Ztg. 1908, **33**, I, 896; Chem. Ztg. Rep. 1908, **32**, 255; Wochenbl. Papfabr. 1908, **39**, 1306; J. S. C. I. 1908, **27**, 562. D. R. P. 207776, 1906; abst. Pap. Fabr. 1909, **7**, I, 293; Pap. Ztg. 1907, **32**, I, 986; J. S. C. I. 1909, **28**, 484; C. A. 1909, **3**, 2072. D. R. P. 216284, 1907; abst. J. S. C. I. 1909, **28**, 1324; Chem.

leathers and nitrocellulose waterproofing compositions, it is

Ztg. Rep. 1909, **33**, 627; Pap. Ztg. 1909, **34**, II, 3716; C. A. 1910, **4**, 1114. U. S. P. 939394, 1909; abst. C. A. 1910, **4**, 527. Chem. Ztg. 1910, **34**, 1352; J. S. C. I. 1911, **30**, 19; C. A. 1911, **5**, 2944. D. R. P. 189177, 1904; abst. Pap. Ztg. 1907, **32**, II, 3356; Chem. Zentr. 1908, **79**, I, 1118; Wochenbl. Papfabr. 1907, **38**, 3049; Wag. Jahr. 1907, **53**, I, 8. Aust. P. 40657, 1906. See D. R. P. 176722, 195286, 199279. A. Kumpfmiller and E. Schultgen, D. R. P. 81388, 83438, 1894; abst. Ber. 1895, **28**, 685; 1896, **28**, 1030. Aust. Privilegium, 5849, 1894. H. Landmark, Nor. P. 21848, 1911; Swed. P. 35500, 1911; Ledertechn. Rundschau, 1912, **4**, 308; Pap. Ztg. 1911, **36**, 3706; 1913, 3063; C. A. 1914, **8**, 2278; Paper, 1913, **13**, No. 11, 23. F. P. 474336, 1914; abst. J. S. C. I. 1915, **34**, 1005. E. P. 7090, 1915; abst. J. S. C. I. 1916, **35**, 372; C. A. 1916, **10**, 2813. Tid. Kemi. Farm. Terapi 1916, **9**, No. 1, 2. F. P. 456871, 1913; Nor. P. 23673, 1912; abst. J. S. C. I. 1913, **32**, 488, 1063; C. A. 1914, **8**, 822; Papir J. 1913, **1**, 15; Paper, 1914, **13**, No. 18, 17. Nor. P. 24562, 1914; abst. Tidschrift, 1914, **4**, 222; Papir J. 1914, 186. Papir J. 1914, **2**, 63; Pulp Paper Mag. Can. 1914, **12**, 267. Papier Ztg. 1915, **40**, 495, 519; Wochenbl. Papfabr. 1915, **46**, 834; 843. Chem. Ztg. 1915, **39**, 98; J. S. C. I. 1915, **34**, 275; C. A. 1915, **9**, 2709; Paper, 1915, **16**, No. 11, 18. U. S. P. 1236948, 1917; abst. C. A. 1917, **11**, 2963; J. S. C. I. 1917, **36**, 1092. Papir J. 1916, **4**, 279; Pulp and Paper Mag. Can. 1917, **15**, 88, 101. Nor. P. 28147, 1917; abst. Papir. J. 1917, **5**, 173. Lassar-Cohn, Pap. Ztg. 1911, **36**, 677. Chem. Ztg. 1914, **38**, 657; abst. J. S. C. I. 1914, **33**, 639; Paper, 1914, **14**, No. 17, 23. D. R. P. Anm. 36157, 1913. R. Laufman, Ledertechn. Rundschau, 1914, **6**, Oct. 22; abst. Collegium, 1915, 106; J. S. C. I. 1915, **34**, 501. Chem. Ztg. 1917, **41**, 273, 286; abst. J. S. C. I. 1916, **35**, 563. A. and E. Lederer, F. P. 464608, 1913; abst. J. S. C. I. 1914, **33**, 478. E. Lehmann, D. R. P. 128661, 1900. 169880, 1905; abst. Pap. Ztg. 1906, **31**, II, 2548. D. R. P. 282950, 282951, 1912; Nor. P. 24561, 1913; abst. C. A. 1915, **9**, 2590; J. S. C. I. 1915, **34**, 656; Wochenbl. Papfabr. 1915, **46**, 1178; Pap. Fabr. 1915, **13**, 314; Papir J. 1914, **2**, 185. C. Leisenberg, D. R. P. 37882, 1886; abst. Ber. 1887, **20**, 30; Pap. Ztg. 1887, **12**, 398. H. Leonhardt, D. R. P. 34420, 1885. K. Leschly-Hansen, Papir J. 1917, **5**. L. Lichtenstein, Chem. Ztg. Rep. 1912, **36**, 658. Farber Ztg. 1913, **24**, 442; Chem. Zentr. 1913, **84**, II, 2181; C. A. 1914, **8**, 2064. H. Liese, E. P. 1832, 1911; abst. J. S. C. I. 1911, **30**, 1441. Lindhardt, Zentr. Oesterr-Ung. Paperind. 1905, 13; abst. Zts. ang. Chem. 1905, **18**, 983. J. Lindsey and B. Tollens, J. C. S. 1889, **55**, 213; Ber. 1893, **26**, 322; J. S. C. I. 1892, **11**, 835. Thesis, Göttingen 1891; Zts. ang. Chem. 1892, **5**, 154; J. S. C. I. 1893, **12**, 287. A. Little, Pap. Fabr. 1907, **5**, 649. E. Ljungberg, Affars varlden, 1912, 133; Pap. Ztg. 1912, **36**, 337, 490. K. Loffl, Seifenseder, Ztg. 1915, **42**, 431; abst. C. A. 1916, **10**, 1443. K. Lorentz, Seifensieder Ztg. 1916, **43**, 400, 501; Zts. ang. Chem. 1916, **29**, 445; J. S. C. I. 1916, **35**, 1163. F. Loveland, J. Amer. Leather Chem. Assoc. 1912, **7**, 368; 1913, **8**, 128; abst. J. S. C. I. 1913, **32**, 373. O. Luhrs, D. R. P. Anm. L. 34995, 1912. A. Luerssen, Zts. Hyg. **58**, 121; abst. J. S. C. I. 1908, **27**, 1220. J. Luke, Nor. P. 26138, 1915; abst. Pap. Fabr. 1915, **3**, 215. Mackay and Miller, J. S. C. I. 1909, **28**, 1183. R. McKee, Pulp, Paper Mag. Can. 1915, **13**, 165. C. Marchand, U. S. P. 1155256, 1915; Can. P. 163400, 1915; abst. C. A. 1915, **9**, 2980, 3358; J. S. C. I. 1915, **34**, 1087. Paper Trade J. 1916, **62**, 201; Paper, 1916, **17**, No. 23, 24. Maschinenbauanstalt Golzern, D. R. P. 69892, 1893; abst. Ber. 1893, **26**, 973; Pap. Ztg. 1893, **18**, 1280. W. Massot, Zts. ang. Chem. 1906, **19**, 177. W. Mathesius, Chem. Ztg. 1913, **37**, 625. Matheus, Pap. Fabr. 1910, **8**, 532; abst. Zts. ang. Chem. 1910, **23**, 1584; Pap. Fabr. 1911, **9**, 1407, 1435; abst. C. A. 1912, **6**, 1365; J. S. C. I. 1911, **30**, 1375, 1446; Pulp Paper Mag. Can. 1912, **10**, 53; Paper 1912, **6**, No. 5, 16. R. McKee, U. S. P. 1273392, 1918; abst. C. A. 1918, **12**, 1926. C.

not as essential that the cellulose-either in the form of a

Melhardt, D. R. P. 148275, 1903; abst. Pap. Ztg. 1904, **29,** I, 574; Wag. Jahr. 1904, **50,** I, 6. H. Messow, D. R. P. 297075, 1915; abst. J. S. C. I. 1917, **36,** 873. L. Meunier, F. P. 466196, 1913; abst. J. S. C. I. 1914, **33,** 604. A. Mitscherlich, D. R. P. 4178, 4179, 1878; 72161, 1891; E. P. 1668, 1882; 12927, 1893; abst. Ber. 1879, **12,** 395; 1894, **27,** 149; J. S. C. I. 1883, **2,** 700; 1894, **13,** 834; Pap. Ztg. 1893, **18,** 3222; 1896, **21,** 2349, 2850. Aust. Privilegium, 112, 1894. E. P. 12566, 1884; 11372, 1890; abst. J. S. C. I. 1885, **4,** 550; 1891, **10,** 787. E. P. 1655, 1884; abst. J. S. C. I. 1885, **4,** 549. D. R. P. 72161, 1891; E. P. 12927, 1893. D. R. P. 72362, 1891; abst. Ber. 1894, **27,** 221; Pap. Ztg. 1894, **19,** 272. D. R. P. 82498, 1893; abst. Ber. 1895, **28,** 869; Pap. Ztg. 1895, **20,** II, 2716. Aust. Privilegium, 112, 1894. D. R. P. 86651, 1895; Add. to D. R. P. 82498, 1893; abst. Ber. 1897, **29,** 452; Pap. Ztg. 1895, **20,** 466, 529; 1896, **21,** II, 1848, 2349, 2850. D. R. P. 93944, 93945, 1896; abst. Pap. Ztg. 1897, **22,** II, 3074, 3148; Chem. Centr. 1897, **68,** II, 1126. D. R. P. 169408, 169409, 1904; abst. Pap. Ztg. 1906, **31,** I, 1732; Wag. Jahr. 1906, **53,** II, 546; Wochenbl. Papfabr. 1906, **37,** 1847, 1848. Holzzellstoffabrikation 1907, 19. D. R. P. 4179, 1878; E. P. 1668, 1882. D. R. P. 4178, 1878. 54206, 1890; Add. to 34420, 1885; abst. Ber. 1891, **24,** 343. D. R. P. 220066, 1908; abst. J. S. C. I. 1910, **29,** 483. 235965, 1911; abst. Pap. Ztg. 1911, **36,** 2077; Pap. Fabr. 1911, **9,** 825; J. S. C. I. 1911, **30,** 1051. Pap. Ztg. 1896, **21,** 2349, 2850. W. Moeller, Collegium, 1913, 489; 1914, 153, 319; abst. C. A. 1914, **8,** 2082; J. S. C. I. 1914, **33,** 365, 654; Ledertechn. Rundschau. 1910, **2,** 73; Pulp Paper Mag. Can. 1914, **12,** 468; Paper, 1914, **14,** No. 19. 18. C. Monnet, Collegium, 1913, 224; abst. Zts. ang. Chem. 1913, **31,** 646; C. A. 1913, **7,** 3856; J. S. C. I. 1913, **32,** 616. H. Moore and R. Wolf, U. S. P. 1103216, 1110454, 1914; abst. C. A. 1914, **8,** 3119; J. S. C. I. 1914, **33,** 859, 1006; Pulp Paper Mag. Can. 1914, **12,** 470, 533; Paper, 1914, **15,** No. 4, 22. E. Morterud, U. S. P. 833936, 1906; D. R. P. 180168, 1905; Aust. P. 638, 1905; abst. C. A. 1907, **1,** 2204; Wochenbl. Papfabr. 1907, **38,** 1056; Pap. Ztg. 1906, **31,** II, 3819; 1907, **32,** I, 296. M. Muller, Wochenbl. Papfabr. 1908, **39,** 1484. D. R. P. 241282, 1910; abst. C. A. 1912, **6,** 2170; J. S. C. I. 1912, **31,** 123; Wochenbl. Papfabr. 1911, **42,** 4864. D. R. P. 262473, 1912. Wochenbl. Papfabr. 1914, **45,** 2276, abst. C. A. 1914, **8,** 3119. P. Muller, E. P. 7324, 1913; abst. J. S. C. I. 1914, **33,** 478; Paper, 1914, **14,** No. 13, 23. Belg. P. 255636, 1913. F. Mullner, D. R. P. 96467, 1897; abst. Chem. Centr. 1897, **68,** I, 1183; Pap. Ztg. 1898, **23,** 687, 1062, 1218. E. Murbe, Swed. P. 41542, 1916; abst. C. A. 1917, **11,** 535. D. R. P. 293394, 1914; abst. J. S. C. I. 1916, **35,** 1106. D. R. P. 297440, 1914; abst. J. S. C. I. 1917, **36,** 870. Necas, Pulp Paper Mag. Can. 1913, **11,** 599; Paper 1913, **12,** No. 10, 20. E. Nemethy, Zentr. Oesterr-Ung. Papierind, 1903, No. 18; Pap. Ztg. 1904, **28,** 1897. E. Neresheimer, Die Wasserwirtschaft, **6,** 2; Wasser Abwasser, 1914, **7,** 408, C. A. 1914, **8,** 1178. A. Nettl, Aust. Privilegium, 1576, 1888. D. R. P. 52491, 1889; abst. Ber. 1891, **24,** 102. A. Nicolle, F. P. 425991, 1910; abst. J. S. C. I. 1911, **30,** 951. P. Nitsche, Wochen. J. amg. Chem. 1912, **43,** 4045; abst. Zts. ang. Chem. 1912, **25,** 2058; C. A. 1913, **7,** 528; J. S. C. I. 1912, **21,** 1000. T. Norton, J. S. C. I. 1911, **30,** 1466; World's Paper Trade Rev. **56,** 1236; C. A. 1912, **6,** 929. J. Novak, D. R. P. 74031, 1893; abst. Ber. 1898, **27,** 474; Pap. Ztg. 1894, **19,** 1196. Oesterreichischer Verein fur Cellulosefabrikation, D. R. P. 104359, 1898; abst. Chem. Centr. 1899, **70,** II, 1077. Oesterreichischer Verein fur Cellulosefabrikation, D. R. P. 180768; abst. Pap. Ztg. 1907, **32,** I, 948. E. Oman, Svensk Pap. Tid. 1916, **19,** 143. Tekn. Tid. 1916, **46,** 6; Pap. Fabr. 1916, **14,** 256, 273, 291, 306, 485, 509, 584; J. S. C. I. 1916, **35,** 832; C. A. 1916, **10,** 2637. Pap. Fabr. 1915, **13,** 534, 553; abst. Zts. ang. Chem. 1915, **28,** 564; J. S. C. I. 1916, **35,** 172; C. A. 1916, **10,** 3158, Chem. Ztg. 1915, **39,** 820; abst. J. S. C. I. 1916, **38,** 172; C. A.

cellulose as cotton, or a lignocellulose as wood pulp, should

1916, **10**, 3158; Paper, 1916, **18**, No. 1, 22. F. P. 481917, 1917; abst. pulp Paper Mag. Can. 1917, **15**, 1197. U. S. P. 1130192, 1915; E. P. 1145, 1914; F. P. 467466, 1914; Can. P. 154165, 1914; abst. C. A. 1914, **8**, 2805; 1915, **9**, 1319, 1843; J. S. C. I. 1914, **33**, 348; 1915, **34**, 419; Pulp, Paper Mag. Can. 1914, **12**, 282; Paper, 1914, **14**, No. 8, 20; 1915, **16**, No. 6, 19. E. P. 103649, 103650, 103651, 103652, 103653, 103654, 103655, 106493, 1917; abst. C. A. 1917, **12**, 1749; Pulp Paper Mag. Can. 1917, **15**, 719, 924. G. Onsager, E. P. 24738, 1913; abst. J. S. C. I. 1915, **34**, 25; Chem. Trade J. 1915, **56**, 355; Paper, 1914, **15**, No. 21, 21; 1915, **16**, No. 7, 12. Opitz and Kayser, Wochenbl. Papfabr. 1908, **39**, 1299. C. Opl, D. R. P. 75351, 1893; abst. J. S. C. I. 1895, **14**, 976. Paeszler, Chem. Ztg. 1906, **30**, 1000; 1912, **36**, 812; J. S. C. I. 1912, **31**, 736. Chem. Ztg. 1914, **38**, 974; abst. J. S. C. I. 1915, **34**, 189; Paper Trade J. 1915, **61**, No. 13, 50. J. Parker, Collegium, 1912, 611; Chem. Ztg. 1913, **37**, 6; C. A. 1914, **8**, 839. E. Partington, Pap. Ztg. 1904, **29**, II, 2686. F. Patch, Paper, 1914, **15**, No. 11, 21. Phelps and McRae, J. S. C. I. 1913, **32**, 389. E. Phelps, The Paper Mill, **32**, 19; Pap. Ztg. 1909, **34**, 726. W. Philippi, D. R. P. 195643, 1904; 211348, 1905; F. P. 369608, 1906; abst. Chem. Zentr. 1908, **79**, II, 1232; 1909, **80**, II, 400; Pap. Ztg. 1908, **33**, I, 1210; 1909, **34**, II, 2294; Wag. Jahr. 1908, **54**, II, 557; J. S. C. I. 1907, **26**, 106; C. A. 1909, **3**, 2640. Aust. P. Anm. 1821, 1909; abst. Chem. Ztg. Rep. 1909, **33**, 447. D. R. P. 254866, 1910; F. P. 448064, 1912; Pap. Fabr. 1913, **11**, 102; J. S. C. I. 1913, **32**, 438, 439. R. Pictet, D. R. P. 26331, 1883. R. Pictet and G. Brelaz, E. P. 9509, 1884; abst. J. S. C. I. 1885, **4**, 464. M. Platsch, D. R. P. 286210, 1911. U. S. P. 1054141, 1913; E. P. 19600, 1912; F. P. 447578, 1912; abst. J. S. C. I. 1913, **32**, 284, 823; C. A. 1913, **7**, 1415. Nor. P. 26028, 1915; abst. Papir J. 1915, **3**, No. **15**, 203. M. Platsch and Hoesch & Co., F. P. 455059, 1913; Norw. P. 26296, 1915; abst. J. S. C. I. 1913, **32**, 864; Pap. Ztg. 1914, **39**, 1988; Papir J. 1915, **3**, 262. E. Pollacsek, Aust. Privilegium, 967, 1898, Aust. Privilegium, 967, 1524, 1898. Aust. Privilegium, 985, 1898. D. R. P. 264783, 1912; 266401, 1913. F. P. 462429, 1913; U. S. P. 1133499, 1915; Nor. P. 24349, 1914; abst. J. S. C. I. 1914, **33**, 248, 746; 1915, **34**, 488; C. A. 1915, **9**, 1391; Papir J. 1914, **2**, 138; Tidskrift, 1914, **4**, 191. Pap. Ztg. 1914, **39**, 1616. H. Polz, Pap. Ztg. 1913, **38**, 3064; Wochenbl. Papierfabr. 1913, **44**, 4611. A. Pritzkow, Eng. Record, 1910, **62**, 468; C. A. 1911, **5**, 1144; Paper, 1912, **7**, No. 1, 23. Mitt. Prufgsamt. Wasser. u Abwassrt. 1911, 119; Chem. Zentr. 1911, **82**, II, 1455. H. Proctor and S. Hirst, J. S. C. I. 1909, **28**, 293; Zts. ang. Chem. 1909, **32**, 1566; C. A. 1909, 2395. J. Puring, U. S. P. 1185604, 1916; abst. C. A. 1916, **10**, 1939; J. S. C. I. 1916, **35**, 747. A. Raaz, Farber Ztg. 1898, **9**, 245; abst. J. S. C. I. 1898, **17**, 923. W. Ramsay, Zts. ang. Chem. 1906, **19**, 833; Chem. Ztg. 1906, **30**, I, 431. F. Raschig, U. S. P. 1056366, 1056367, 1913; E. P. 2069, 11568, 29696, 1912; F. P. 440625, 447419, 1912; abst. J. S. C. I. 1913, **32**, 454, 845. H. Reed, U. S. P. 1217218, 1917; abst. J. S. C. I. 1917, **36**, 503; C. A. 1917, **11**, 1545. A. Reilley, U. S. Com. Repts. No. 276, Nov. 24, 1917, 755. B. Reinitzer, Pap. Ztg. 1911, **36**, 2882, 2913; Zts. ang. Chem. 1911, **24**, 1851; J. S. C. I. 1911, **30**, 1206; Oesterr. Chem. Ztg. **15**, 61; C. A. 1912, **6**, 1480. P. Remy, D. R. P. 90798, Pap. Ztg. 1897, **22**, 426; J. S. C. I. 1897, **16**, 630. A. Richter, D. R. P. Anm. R, 31311, 1910. D. R. P. 275832, 1910; abst. Pap. Ztg. 1914, **39**, 2021; J. S. C. I. 1914, **33**, 1043. A. Richter and L. Dunbar, U. S. P. 1213414, 1213415, 1917; abst. C. A. 1917, **11**, 888. E. Rinman, D. R. P. 269994, 1913; abst. J. S. C. I. 1914, **33**, 346. Wochenbl. Papfabr. 1915, **46**, 990; Chem. Ztg. 1915, **39**, 99; J. S. C. I. 1915, **34**, 274; Pap. Ztg. 1915, **40**, 559, 574; C. A. 1915, **9**, 2709; Paper 1915, **16**, No. 9, 11; Pulp, Paper Mag. Can. 1915, **13**, 337. Nor. P. 26603, 1914; Swed. P. 42108, 1917; Papir J. 1916, be as thoroughly and exhautively purified, as some of nitro-

4, 47; C. A. 1917, **11,** 2153; Pulp Paper Mag. Can. 1917, **15,** 741. J. Robeson, E. P. 17956, 1908; Aust. P. 42479, 1906; abst. Pap. Ztg. 1905, **30,** I, 266; C. A. 1910, **4,** 669. U. S. P. 833634, 1906; E. P. 22887, 1906; abst. J. S. C. I. 1906, **25,** 1115; 1907, **26,** 340; C. A. 1907, **1,** 498. U. S. P. 851378, 851379, 851380, 851381, 1907; abst. J. S. C. I. 1907, **26,** 634; C. A. 1907, **1,** 1640. E. P. 17956, 17957, 17958, 1908; U. S. P. 851378, 851379, 851380, 851381, 1909; Aust. P. 42479, 1909; Chem. Ztg. 1907, **31,** 312; Pap. Ztg. 1910, **35,** 300; J. S. C. I. 1909, **28,** 1052. U. S. P. 947101, 1909; 947128, 1910; abst. C. A. 1910, **4,** 652. J. Robeson, Aust. P. 42479. Paper, 1911, **8,** No. 9, 63. U. S. P. 1013614, 1912; D. R. P. 238119, 1907; Pap. Ztg. 1913, **38,** 1221; C. A. 1912, **6,** 591, 1592. U. S. P. 1069031, 1913; abst. J. S. C. I. 1913, **32,** 864. U. S. P. 1069029, 1069030, 1069031; 1075856, 1075857, 1913; abst. J. S. C. I. 1913, **32,** 864, 869, 1070. J. Rogers, Paper Trade Rev. 1904, **31,** No. 12. P. Rohland, Farber. Ztg. 1913, **24,** 401; Pap. Ztg. 1913, **38,** 3522. Chem. Ztg. 1913, **37,** 754. Biochem. Zts. 1912, **46,** 374; abst. J. S. C. I. 1912, **31,** 1119. Zts. ang. Chem. 1913, **80,** 174; Chem. Zentr. 1913, **84,** I, 1858. Rosenblatt and M. Rosenband, Chem. Ztg. 1909, **33,** 921. Rosenthal, Pap. Ztg. 1914, **39,** 1007; Wochenbl. Papfabr. 1914, **45,** 1847; Chem. Ztg. 1914, **38,** 126. Sachs-Bankges, Quellmalz & Co., D. R. P. 158497, 1906; 186652, 1907. E. Sandberg and G. Sundblad, E. P. 24125, 1912; abst. J. S. C. I. 1913, **32,** 279; C. A. 1914, **8,** 1346. A. Sander, Fort. Chem. 1911, **4,** 300. J. Saxl and L. Oberländer, D. R. P, 63042, 1891; abst. Zts. ang. Chem. 1892, **5,** 382. C. Schall, D. R. P. 194127, 194744, 194745, 196390, 197160, 197587, 201052, 202393, 204470, 206743, 206999, 207355, 208373; abst. Zts. ges. Wasserwirtsch, 1909, **9,** 147. H. Schild, Pap. Ztg. 1900, **25,** I, 1725; II, 1125, 2456; Jahr. Chem. 1900, **53,** 15. J. Schlauf, Paper Maker Brit. Trade J. 1911, **42,** 55. A. Schmidt, U. S. P. 1136723, 1915; abst. C. A. 1915, **9,** 1526. H. Schmidt, D. R. P. 86542, 1895; abst. Ber. 1896, **29,** 452. S. Schmidt-Nielsen, Papir J. 1916, **4,** 17. H. Schnarmann, Pap. Ztg. 1897, **22,** II, 3679. F. Schneider, Pap. Ztg. 1910, **35,** 1902; Zts. Hyg. 1907, 121; Pap. Fabr. 1909, **7,** 34; Zts. ang. Chem. 1909, **22,** 655. Collegium, 1912, 678. F. Schneider and G. Graf, D. R. P. Anm. Sch. 36744, 1910; abst. Pap. Fabr. 1911, **9,** 827. R. Schorr, Eng. Min. J. 1910, **88,** 451; C. A. 1910, **4,** 1369. H. Schrieb, Pap. Ztg. 1888, **12,** 1489; 1889, **14,** 1576, 1875. Zts. ang. Chem. 1890, **3,** 675. Pap. Ztg. 1906, **30,** 1111; Zts. ang. Chem. 1906, **19,** 1302. Chem. Ztg. 1907, **31,** 1133, 1157; abst. Zts. ang. Chem. 1907, **20,** 1986. F. Schulte, Ledertechn. Rundschau, 1914, **6,** 129; abst. C. A. 1914, **8,** 2637; J. Amer. Leather Chem. Assoc. 1914, **9,** 335. G. Schutz, D. R. P. Anm. Sch. 39465, 1911. J. Schwager, Pap. Ztg. 1903, **28,** II, 2075, 2183. C. Schwalbe, Wochenbl. Papfabr. 1910, **41,** 2354; Zts. ang. Chem. 1910, **23,** 1080, 1537; J. S. C. I. 1910, **29,** 1052; Pap. Ztg. 1910, **35,** 2004; C. A. 1911, **5,** 196. Koll. Zts. 1909, **5,** 129. C. Schwalbe and H. Grim, Wochbl. Papfabr. 1913, **44,** 3251; C. A. 1913, **7,** 3837. J. Scott, Paper Maker Brit. Trade J. 1914, **47,** 395; abst. C. A. 1914, **8,** 2620. Paper Maker Brit. Trade J. 1911, **42,** No. 3, 401; Wasser Abwasser, 1911, **4,** 540. B. Segerfeld, Pap. Ztg. 1910, **35,** 2518, 2558. H. Seidel, Mitth. Tech. Gew. Mus. 1897, **7,** 119; abst. J. S. C. I. 1898, **17,** 178. Zts. ang. Chem. 1900, **23,** 1307; Pap. Ztg. 1900, **25,** II, 3295; J. S. C. I. 1900, **19,** 1033. Rev. gen. mat. Col. 1898, **2,** 370; abst. J. S. C. I. 1898, **17,** 1048; Pap. Ztg. 1898, **23,** II, 2812; Chem. Ztg. 1898, 665. Farber Ztg. 1899, **10,** 68. Mitt. Techn. Gew. Mus. 1900, **10,** 158; abst. J. S. C. I. 1900, **19,** 896. H. Seidel and L. Hanak, Mitt. Techn. Gew. Mus. 1898, **8,** 337; abst. J. S. C. I. 1898, **17,** 863. H. Seidel and L. Hanak, Mitt. Techn. Gew. Mus. 1898, **8,** 337; abst. J. S. C. I. 1898, **17,** 863. H. Seidel and J. Pollak, Farber Ztg. 1899, **10,** 321; abst. Wag. Jahr. 1899, **49,** 972. W. Sembritzki, Wochenbl. Papfabr. 1908, **39,** 658, 2866; Chem. Ztg. Rep. 1908, **32,** 221; J. S. C. I. 1908, **27,** 466, 915;

cellulose used for lacquers and in the fabrication of artificial

Pap. Ztg. 1908, **33,** 872; C. A. 1908, **2,** 484, 1885, 3463; Pulp, Paper Mag. Can. 1908, **6,** 257. Pap. Ztg. 1908, **33,** I, 872; Wochenbl. Papfabr. 1908, **39,** 2866; J. S. C. I. 1908, **27,** 915; C. A. 1908, **2,** 3403. Shelvin and Small, U. S. P. 880247, 1908; abst. Chem. Ztg. Rep. 1908, **32,** 347. E. Siebner, Chem. Ztg. 1913, **37,** 1057. Simonson, Swed. P. 28551, 1907. R. Sindall, Paper Makers Monthly J. 1911, **39,** 401; Pap. Ztg. 1912, **36,** 300; Pulp Paper Mag. Can. 1912, **10,** 59. F. Small, J. Amer. Leather Chem. Assoc. 1913, **8,** 62; Zts. ang. Chem. 1913, **26,** 670. B. Smart, Swed. P. 31956, 1909; abst. C. A. 1912, **6,** 2316. L. Sody, Chem. Ztg. 1913, **37,** 442; abst. Collegium, 1912, 529; J. Amer. Leather Chem. Assoc. 1912, **7,** 373; J. S. C. I. 1912, **31,** 737. Sollbrig, Pap. Fabr. 1907, **5,** 5. K. Sorge and A. Weiskopf, Chem. Ztg. 1913, **37,** 7. H. Spatz, D. R. P. 159377, 1903; abst. Wag. Jahr. 1905, **51,** I, 379; Pap. Ztg. 1905, **30,** 1054. H. Spindler, Chem. Ztg. 1897, **21,** 302. A. Splittgerber, Wasser u Gas. 1914, 243, 268, 290, 313; Wasser Abwasser, 1914, **7,** 24; C. A. 1915, **9,** 376. D. Stewart, Aust. P. 40528, 1907; U. S. P. 909343, 1909; abst. Chem. Ztg. 1909, **33,** 175. Stora Kopparbergs Aktiebolag, F. P. 402331, 1909; abst. J. S. C. I. 1909, **28,** 1221; Wochenbl. Papfabr. 1909, **40,** 4265; Pap. Ztg. 1909, **43,** 1682. D. R. P. 256964; abst. Pap. Ztg. 1913, **37,** 768; Pap. Fabr. 1913, **11,** 342; J. S. C. I. 1913, **32,** 421; C. A. 1913, **7,** 2472. R. Strehlenert, U. S. P. 1149420, 1915; D. R. P. 266096, 1912; Can. P. 151445, 1913; Nor. P. 24140, 1912; Swed. P. 34941, 1912; abst. C. A. 1914, **8,** 572; J. S. C. I. 1913, **32,** 1104; 1914, **34,** 957; Paper, 1915, **17,** No. 2, 19; Paper Trade J. 1916, **63,** 64; Pap. Fabr. 1913, **9,** 666. Pulp, Paper Mag. 1913, **11,** 452; abst. C. A. 1913, **7,** 3022. Svensk Kem. Tid. 1913, **25,** 78; Pap. Fabr. 1913, **11,** 645, 666; C. A. 1913, **7,** 2471; J. S. C. I. 1913, **32,** 652; Pulp, Paper Mag. Can. 1913, **11,** 778; 1914, **12,** 46; Paper, 1913, **12,** No. 9, 18; Chem. Ztg. Rep. 1913, **37,** 605; Wochenbl. Papfabr. 1913, **44,** 4142. Pap. Ztg. 1914, **39,** 414. Papir J. 1916, **4,** 269; abst. Pulp, Paper Mag. Can. 1917, **15,** 88, 101; Papir J. 1917, **5,** 14; abst. Pulp, Paper Mag. Can. 1917, **15,** 449. Paper Trade J. 1917, **45,** 36; Paper Makers Monthly J. 1917, **55,** 284; Pulp Paper Mag. Can. 1917, **15,** 1073. J. I. E. C. 1916, **8,** 1070. Nor. P. 27637, 1917; abst. Pulp, Paper Mag. Can. 1917, **15,** 789. Svensk Pap. Tid. 1917, **20,** 128, No. 12, 144; No. 13, 158. Papir J. 1917, **5,** 101; abst. Pulp, Paper Mag. Can. 1917, **15,** 764. A. Stutzer, W. Landw. Presse, 1902, **29,** 725; Chem. Ztg. Rep. 1902, **26,** 327; J. S. C. I. 1903, **22,** 42. Chem. Ztg. 1910, **34,** 1167; J. S. C. I. 1910, **29,** 1370; Wochbl. Papfabr. 1910, **41,** 4148; C. A. 1911, **5,** 1335. Pap. Ztg. 1911, **35,** 5; Jahr. Chem. Techn. 1913, II, 501. D. R. P. 215273, 1908; abst. Pap. Ztg. 1909, **34,** II, 3758; Chem. Zentr. 1909, **80,** II, 1783. Zts. ang. Chem. 1909, **22,** 1999; abst. C. A. 1910, **4,** 107; J. S. C. I. 1909, **28,** 1162; Pap. Ztg. 1909, **34,** II, 3210, 3251; Wochenbl. Papfabr. 1909, **40,** 107. F. P. 402871, 1909; abst. J. S. C. I. 1909, **28,** 1323. Chem. Ztg. 1910, **34,** 1352; abst. C. A. 1911, **5,** 2946; J. S. C. I. 1911, **30,** 18. D. Landw. Presse 1902, No. 63. J. S. C. I. 1913, **32,** 1165. Wochenbl. Papfabr. 1913, **42,** 2685; Landw. Ztg. 1913, **62,** 139; C. A. 1913, **7,** 4037; Pulp, Paper Mag. Can. 1913, **11,** 769; Paper, 1913, **11,** No. 8, 22. D. R. P. 256658, 1911; abst. Zts. ang. Chem. 1912, **25,** 1752; J. S. C. I. 1912, **31,** 871. Pap. Ztg. 1911, **36,** 3450. D. R. P. 236035, 1909; abst. Pap. Fabr. 1911, **9,** 858; C. A. 1911, **5,** 3622. Pap. Ztg. 1911, **36,** 3738; Wochenbl. Papfabr. 1911, **42,** 4956; C. A. 1912, **6,** 1850; J. S. C. I. 1912, **31,** 121. D. R. P. 246658, 1911; abst. C. A. 1912, **6,** 2529. Sudenburger Maschinenfabrik u Eisengisserei, D. R. P. 219204, 266909, 1912. A. Sweinburg, Aust. P. 14423, 1902. J. Szamek, D. R. P. 130665, 1901; abst. Bied. Chem. Tech. Jahr. 1901, 590; Chem. Centr. 1902, **73,** I, 1082. H. Tartar, J. Ind. Eng. Chem. 1916, **8,** 226; abst. J. S. C. I. 1916, **35,** 483; C. A. 1916, **10,** 1268; Paper, 1916, **17,** No. 26, 14. A. Tavernier and C. Oulman, F. P. 359239, 1905; D. R. P. 186775, 1906; abst.

filaments, or for transparent thermoplastic celluloid compounds. Wochenbl. Papfabr. 1907, **38,** 3048; Chem. Zentr. 1907, **78,** II, 1276; J. S. C. I. 1906, **35,** 365. F. P. 413152, 1910; abst. J. S. C. I. 1910, **29,** 1095. W. Teas, U. S. P. 916057, 1909; abst. J. S. C. I. 1909, **28,** 432. C. Thorne, U. S. P. 1076078, 1912; D. R. P. 291854, 1913; Nor. P. 26445, 1915; abst. C. A. 1917, **11,** 1546; Papir J. 1916, **4,** 22; Pulp Paper Mag. Can. 1917, **15,** 677. Pulp Paper Mag. Can. 1915, **13,** 173; abst. C. A. 1915, **9,** 1390. B. Tilghman, E. P. 2924, 1866; U. S. P. 70485, 1867; 92220, 1869. E. Tillberg, Swed. P. 25283, 1907. E. Trainer, D. R. P. 136322, 140542, 140862, 144819, 161675; abst. Chem. Centr. 1902, **73,** II, 410; Pap. Ztg. 1902, **27,** II, 3478; 1903, **28,** II, 1942, 3086; 1905, **30,** II, 2582; Wag. Jahr. 1903, **49,** 16, 162; 1905, **51,** I, 19; Wochenbl. Papfabr. 1903, **34,** 2658; Pap. Fabr. 1903, **1,** 419; 1905, **3,** 1557. D. R. P. 239675, 1909; Zts. ang. Chem. 1912, **24,** 2335; C. A. 1912, **6,** 2169. D. R. P. 181126, 1905; abst. Pap. Ztg. 1907, **32,** 994; Wochenbl. Papfabr. 1907, **38,** 1307; J. S. C. I. 1907, **26,** 1272. Pap. Fabr. 1907, 641. Pap. Ztg. 1907, **32,** 994; Chem. Zentr. 1907, **78,** II, 109. D. R. P. 197195, 1906; Aust. P. 36847, 1908; abst. J. S. C. I. 1908, **27,** 708; Chem. Zentr. 1908, **79,** I, 1595; Pap. Ztg. 1908, **33,** I, 1516; Zts. ang. Chem. 1908, **21,** 2539; C. A. 1908, **2,** 2301. D. R. P. 202132, 1907; abst. Chem. Zentr. 1908, **79,** II, 1389; Wochenbl. Papfabr. 1908, **39,** 3238; J. S. C. I. 1908, **27,** 1173; C. A. 1909, **3,** 491. D. R. P. 283931, 1911; abst. C. A. 1915, **9,** 2591, U. S. P. 974001, 1910; abst. J. S. C. I. 1910, **29,** 1365, and W. Haage, U. S. P. 969504, 1910; abst. J. S. C. I. 1910, **29,** 1365. W. Trippe, E. P. 8088, 1901; abst. J. S. C. I. 1901, **20,** 741. D. R. P. 133312, 1901; abst. Chem. Centr. 1902, **73,** II, 410. G. Turk, D. R. P. 115607, 1899; abst. Wag. Jahr. 1900, **46,** II, 530. H. Ullmann, Aust. Privilegium, 3043, 1890. F. Ulzer and H. Seidel, Mitt. Techn. Gew. Mus. 1896, **6,** 186. Voerkelius, Wochenbl. Papfabr. 1911, **42,** 853. J. Vogel, Zts. ang. Chem. 1906, **19,** 748, 750; 1907, **20,** 786; Wochenbl. Papfabr. 1907, **38,** 780, 881, 958; Pap. Ztg. 1906, **31,** 1278, 1314, 1355; 1907, **32,** 961, 1010, 1054, 1098; Chem. Zentr. 1906, **77,** I, 1853. Pulp Paper Mag. Can. 1907, **5,** 142. Wochenbl. Papfab. 1906, **37,** 1612; Pap. Ztg. 1906, **31,** 1278, 1314, 1355; J. S. C. I. 1906, **25,** 555. Pap. Ztg. 1908, **33,** II, 3855, 3890, 3931; Wochenbl. Papfabr. 1909, **40,** 847, 930; Zts. ang. Chem. 1909, **22,** 49; J. S. C. I. 1909, **28,** 158; C. A. 1909, **3,** 1196; Pulp, Paper Mag. Can. 1909, **7,** 289. Pap. Ztg. 1909, **34,** I, 3; abst. Zts. ang. Chem. 1910, **23,** 116; Chem. Ztg. 1909, **33,** 1187. Pap. Ztg. 1911, **35,** 1547; abst. C. A. 1912, **6,** 803. Pap. Fabr. 1911, **9,** 438; abst. J. S. C. I. 1911, **30,** 532; C. A. 1911, **5,** 2520. K. Voitel, Rauch Staub. 1912, **2,** 252; Wasser Abwasser 1913, **6,** 144; C. A. 1913, **7,** 692. B. Wagner, D. R. P. 188428, 1906; abst. Pap. Ztg. 1907, **32,** II, 3356; Wochenbl. Papfabr. 1907, **38,** 3579; Wag. Jahr. 1907, **53,** I, 10. W. Walker, J. S. C. I. 1913, **32,** 389; Chem. Eng. 1913, **17,** 246. J. S. C. I. 1913, **32,** 389; Paper, 1913, **11,** No. 9, 21. J. Wallin, D. R. P. 246708, 1908; abst. C. A. 1912, 2569. Nor. P. 18687, 1908; abst. Chem. Ztg. Rep. 1909, **33,** 251; Pap. Ztg. 1910, **35,** No. 16; Chem. Zentr. 1912, **83,** I, 1871; Pulp Paper Mag. Can. 1912, **10,** 358. Pap. Ztg. 1910, **35,** 1588, 2519; Wochenbl. Papfabr. 1909, **40,** 4253. Pap. Ztg. 1912, **36,** 1283. Pulp Paper Mag. Can. 1913, **11,** 526. J. Walsh, U. S. P. 1178979, 1916; abst. J. S. C. I. 1916, **35,** 636. R. von Walther, D. R. P. 262468, 1912; abst. J. S. C. I. 1913, **32,** 827. M. Webster, Pap. Ztg. 1889, **14,** 1312. A. Wegelin, Akt. Ges. f. Russfabrikation, F. P. 474819, 1914; abst. J. S. C. I. 1915, **34,** 1118. F. Weld, J. Lindsey, W. Schnelle and B. Tollens, Ber. 1890, **23,** 2990; abst. J. S. C. I. 1891, **10,** 156. R. Weldert, Gesund. Ing. 1909, **32,** 723; Chem. Ztg. Rep. 1909, **33,** 617; Pap. Ztg. 1910, **35,** 300. F. Wellensick, D. R. P. 266998, 1913; abst. J. S. C. I. 1914, **33,** 39. J. Welsh, U. S. P. 1175853; abst. Paper, 1916, **18,** No. 2, 14. E. Wernecke, D. R. P. 201372, 1907. H. Wichelhaus, Chem. Ind. 1895, **18,** 51; Pap. Ztg. 1895, **20,** 1180; Chem. Ztg. 1895, **19,** 46. H. Winter, Ledertechn.

As S. Wells and V. Edwardes have pointed out,[1] the woods of the deciduous trees are considerably inferior to those from coniferous trees as raw materials for the manufacture of cellulose suitable for nitration. The inferiority is based mainly on the high percentage of pentosans in the cellulose and on the extreme shortness of the fibers of the former group. In the manufacture of wood cellulose the most difficult point to meet in the specification is that which requires a solubility in 10% potassium hydroxide solution not exceeding 7%. Soda wood pulp manufactured from jack pine in the unbleached condition, prepared by rapid digestion by severe treatment, came within the limits of specification, but after bleaching, the amount of matter soluble in caustic alkali was increased to an abnormal extent, so that the specification could not be met when more than 5% of bleaching powder was employed. That amount, however, is quite inadequate for bleaching a soda wood pulp, so that the authors recommend the use of soda pulp only in the unbleached condition, and consider the caramelized brown coloring matters as probably innocuous for explosives manufacture. Sulfite pulp, on the other hand, does not form products soluble in caustic alkali as the result of moderate bleaching, but it contains a large amount of such matters originally. By digesting sulfite pulp with weak caustic soda under mild conditions, matters soluble in alkali are removed, but the pulp suffers a loss of about 25% in weight. Sulfite pulp so treated is sufficiently pure to pass the nitration tests without bleaching, but if a good color be required it may be bleached satisfactorily with 4% of bleaching powder. Batches both of soda pulp and purified sulfite pulp in the form of crêped sheets have been submitted to nitration with distinctly satisfactory results. The sheets nitrated evenly, yielding products with high solubility in ether-alcohol, and a high nitrogen content. The

Rundschau. 1913, **5**, 161; abst. Zts. ang. Chem. 1913, **26**, 646. A. Winthol, D. R. P. 287016, 1913; abst. J. S. C. I. 1916, **35**, 103. F. Wolesky, Pap. Ztg. 1914, **39**, 1008. L. Woodrop, U. S. P. 1221259, 1917; abst. J. S. C. I. 1917, **36**, 540. J. Yocum and A. Faust, J. Amer. Leather Chem. Assoc., 1911, **6**, 537; J. S. C. I. 1912, **31**, 36; Collegium, 1912, 227; Chem. Ztg. 1913, **37**, 115. Zawadski and Meyer, D. R. P. 45951, 1888; Aust. Privilegium, 1210, 1889; abst. Ber. 1889, **22**, 75. A. Ziegler, D. R. P. 105669, 1897; abst. Chem. Ztg. 1900, **25**, I, 154.

[1] Paper, 1919, **23**, 180; abst. J. S. C. I. 1919, **38**, 603-A; C. A. 1919, **13**, 3012.

sulfite pulp gave a little trouble in the wringers on account of the clogging of the holes. The nitrocellulose from the wood pulp occupied more space in the boiling tubs than that from cotton but it was ground in half the time in the hollanders. The wood pulp product was not so easily dehydrated as that from cotton. It was less viscous than nitro-cotton and a saving of 10% in solvent was recorded. Yields of nitrocellulose from wood pulp in the laboratory showed 150%, as compared with 160%-165% from cotton.[1]

W. Baker[2] has called attention to the fact that waxy and resinous impurities present in wood pulp tend to form yellow compounds on nitration which have an adverse influence on the stability. The yellow compounds are partly eliminated by prolonged boiling with water, preferably with the addition of a little sodium carbonate. The presence of hydrocellulose or oxycellulose in the wood pulp is also highly deleterious from the point of view of

---

[1] As a result of the investigation, material that met the specifications for cotton was thus obtained from both soda and sulfite pulps. Fifty pound batches, together with one of sulfate pulp, were sent to the Picatinny Arsenal, where the nitrating investigations on wood pulp are being conducted by the Ordnance Department. Runs were made using the factory nitrating apparatus with acid mixtures found by the Arsenal staff to be very successful with wood pulp and the product carried through the regular steps used in the plant and run into powder of several calibers.

Contrary to expectations, the soda and treated sulfite sheets nitrated very evenly with a high solubility in ether-alcohol and a high nitrogen content. The solubility of the sulfate pulp was not so good but it seems probable that, with a few trials, this fault can be remedied.

The soda and sulfate pulps wrung easily, but trouble to some extent was experienced with the sulfite on account of plugging of the holes of the wringer.

In the boiling tubs the weight of the nitrocellulose contents were reduced by 40% on account of the greater volume taken by wood pulp over that of an equal weight of cotton.

In the pulping operation, however, wood pulp was reduced in half the time taken for cotton with a corresponding decrease in power and increase in capacity.

The poaching treatment was also cut in half, due to the greater accessibility of the interior of the fiber canals of wood pulp to water in comparison with the very fine canals of cotton.

It was found to take longer in the wringers to wring wood pulp to the same moisture content, probably due to the relatively larger volume of the fiber canals.

More time or pressure also was necessary in the dehydrating presses.

In mixing, wood pulp was found to be less viscous and a saving of 10% in solvent was possible.

In the graining presses no difference was noticeable except that due to the difference in viscosity.

[2] Pulp and Paper Ind. 1918, 45.

stability, and the products of the chlorine bleach are very detrimental. The mineral constituents of the pulp, especially the silica, should be reduced to a minimum. Vegetable wax and resins present a resistance to the uniform penetration of the nitrating acids which is inimical to successful nitration; for this reason the ether-extract of the cellulose should not exceed 0.4%. The physical condition of the cellulose is of the greatest importance; the texture and length of fibers should be as uniform as possible. The yield of nitrated product is considerably reduced by the presence of modified cellulose which is soluble in the acids. For this reason bleached soda pulp gives results greatly inferior to sulfite pulp. The suitability of a pulp from this point of view may be determined by the loss of weight when boiled with a 10% solution of potassium hydroxide. Samples of wood pulp specially manufactured in Germany for the preparation of explosives have been examined and nitrated on the large scale, and the nitrocellulose obtained was in every respect equal to similar products prepared from cotton.

C. Schwalbe and A. Schrimpff[1] have examined a variety of wood celluloses—Mitscherlich cellulose, Ritter-Kellner cellulose, soda cellulose, aspen cellulose—were compared with paper and cotton wool as regards suitability for making guncotton. The chemical properties before nitration were determined. After nitration, solubility, stability, nitrogen content, etc., were estimated. All the wood celluloses yielded stable nitro products, but the nitrogen contents were lower, solubilities higher, yields lower, and nitric acid consumption higher than with cotton wool under the same conditions. To obtain the same nitrogen content a stronger nitric acid is necessary. Specifications for celluloses for nitration should include limits for moisture, ash, portion soluble in alcohol and ether, lignin, oxycellulose. Absence of chlorine compounds and a good absorptive power for nitrating acids are prescribed.

They have also[2] made comparative nitration experiments with cotton and a series of typical wood celluloses. The commercial wood pulps were transformed into thin sheets of paper,

---

[1] Zts. Schiess. Sprengst. 1919, **14**, 41; abst. Chem. Zentr. 1919, **90**, II, 622; J. S. C. I. 1919, **38**, 555-A.

[2] Zts. ang. Chem. 1914, **27**, 662; abst. J. S. C. I. 1915, **34**, 152; C. A. 1915, **9**, 715. See also O. Witt, Chem. Ztg. 1914, **38**, 120.

which were dried at 95°–100° before nitration. The highest nitrate obtained from cotton contained 13.46% N, the highest from wood cellulose 13.34%. It was found possible to prepare from wood pulp a nitrocellulose with a solubility of 5%–6% in ether-alcohol. Stabilization by digestion with water under pressure produced a change in the constitution of the nitrocellulose such that its solubility in ether-alcohol was materially increased; the ordinary technical method of stabilization was therefore adopted. No difficulty was experienced in removing the unstable products from the nitrocelluloses prepared from wood pulp; after suitable treatment these gave results conforming with the official specification by Bergmann and Junk's test, and were at least as stable as the cotton nitrocelluloses. In the nitration of thin paper, success depends on the structure of the latter: overbeaten fibers give bad results. In pulping nitrocotton, traces of copper, amounting in some cases to 0.050%–0.058%, may be absorbed from the beater-knives, but without appreciable effect upon the stability test. In celluloid manufacture, the product is sometimes bleached after nitration and pulping; this operation was found to eliminate unnitrated cellulose and had a slight effect on the nitrogen-content, varying in either direction according to the origin of the material. Unstable sulfuric esters can be eliminated by boiling with dilute acid; 1% hydrochloric acid gave better results than dilute sulfuric acid, causing no decomposition of the nitrocellulose, and leaving a product of lower solubility and somewhat greater stability.

K. Nitzelnadel[1] has prepared nitrocellulose from various samples of sulfite wood pulp, bleached and unbleached, also from straw cellulose. These materials contain higher proportions of non-cellulose impurities than the cotton ordinarily employed in the nitrocellulose industry; straw pulp also possesses the disadvantage of not being readily wetted by liquids. The nitration experiments showed that sulfite wood pulp yields products containing at least as much nitrogen as those prepared from cotton; the products from straw cellulose were generally rather poorer in nitrogen. The solubility in ether-alcohol of the nitrocellulose

---

[1] Wochenbl. Papierfabr. 1912, **43**, 3488; abst. J. S. C. I. 1912, **31**, 954; Zts. Schiess Spreng. 1912, **7**, 257, 301, 339, 384, 409; abst. C. A. 1913, **7**, 257, 892; J. S. C. I. 1912, **31**, 954; Chem. Zentr. 1912, **83**, II, 157; Chem. Tech. Rep. 1912, **36**, 507; Wag. Jahr. 1912, **58**, I, 438.

prepared from these celluloses was generally over 40%; in one case only was it as low as 13%. The films obtained on evaporating the solutions were inferior to those from solutions of nitrated cotton. The stability tests, performed according to Will's method, showed that these nitrocelluloses were sufficiently stable to satisfy official specifications; the products from straw cellulose showed the lowest stability. The ignition temperature, according to Kast's test, was in general somewhat lower than for nitrated cotton, but all the nitrocelluloses prepared from wood fiber showed temperatures of ignition well above the specified minimum limit of 180°; the products from straw cellulose tended to fall below this limit. The yields of nitrocellulose from sulfite wood pulp were lower than those obtained from cotton; straw cellulose gave the lowest yields. The author's conclusions are in favor of the use of wood cellulose as a raw material in the nitrocellulose industries, but he considers straw cellulose unsuitable. The disadvantages of wood cellulose, as compared with cotton, are the lower yields, the lower ignition temperature of the products and the greater solubility in ether-alcohol. Commenting on the above, Klemm points out that one of the chief difficulties in preparing nitrated derivatives from wood cellulose lies in the different structure of the cells of the spring and autumn growths, and it is possible that woods grown in tropical regions would afford more uniform results under chemical treatments.

In the process of W. v. Ruckteschell,[1] wood fiber is boiled with potash and with dilute nitric acid, and after drying is then considered in proper condition for nitration. The Zellstoffabrik Waldhof[2] purify lignin by treatment with calcium sulfite solution, bleaching with calcium hypochlorite, washing with dilute caustic potash solution and purifying with alcohol. The last treatment, although it is said to leave the lignin practically resin-free, is unduly expensive.

In another more recent method,[3] wood in any form is first treated with Schweizer's reagent, then with liquid ammonia,

---

[1] E. P. 4349, 1886. The product is chiefly for use in actuating the gas engine described in E. P. 15475, 1885.

[2] D. R. P. 64878; abst. Wag. Jahr. 1892, **38**, 371; Ber. 1893, **26**, 78; Zts. ang. Chem. 1892, **5**, 706.

[3] D. Whitehead and Q. Marino, E. P. 20143, 1905; abst. J. S. C. I. 1906, **25**, 1052; Chem. Zts. 1906, **5**, 572.

being finally washed free from alkali with water and dried. For bleaching the lignin, treatment with SO_2 gas is specified. P. Girard[1] eliminates resins, gums and other non-cellulose products in wood by extracting the wood pulp in the disintegrated or sheet form with a volatile solvent which, while not attacking the lignin portion, readily dissolves the resins. Solvents specified as suitable are alcohols, acetone, carbon tetrachloride and the chlorinated derivatives of ethylene and ethane. The solvents are preferably employed in conjunction with 5%–10% of commercial aqueous formaldehyde. The essence of the C. Classen process[2] is to first dry the wood pulp, which is then rolled up tightly or compressed, and the products then comminuted in a wood-working machine. In this manner, it is alleged, an entirely uniform product especially suitable for esterification is obtained.

In the nitration of wood cellulose to a product especially applicable for the manufacture of celluloid, K. Schonlau[3] takes wood cellulose, manufactured either by the sulfite or sulfate processes, which is first bleached and then treated in a beating engine with a mixture of water and oil of turpentine to remove the resins and other incrusting matters. The cellulose is then made into a cellulose wadding formed of thin layers, which is dried at a moderate temperature and is then suitable for nitration.

V. Edwardes[4] has described a process whereby vegetable fibrous materials such as wood-chips are treated with acid sulfite liquor, the fibrous material being separated from the liquor and treated with a 0.5%–2% solution of NaOH under a pressure of at least ten pounds per square inch, and at a temperature of at least 115°. In this manner, it is claimed, a cellulose especially suitable for nitration is obtained.

W. Baker[5] has called attention to the fact that substances foreign to normal cellulose are undesirable in cellulose for conversion into cellulose nitrates because of their interference with (1) the stability of the resulting nitrate, (2) the adaptability to a specific use and (3) the yield of finished products. The stability

---

[1] F. P. 443897, 1912; abst. J. S. C. I. 1912, **31,** 1120; Kunst. 1913, **3,** 15.

[2] Swiss P. 71591, 1916; abst. C. A. 1916, **10,** 1791.

[3] F. P. 469484, 1914; abst. J. S. C. I. 1915, **34,** 24.

[4] U. S. P. 1310694, 1919; abst. C. A. 1919, **13,** 2443.

[5] Tech. Assoc. Pulp and Paper Ind. 1918, 45; abst. C. A. 1919, **13,** 3012.

of the resulting nitrates is decreased by the presence in the cellulose of vegetable waxes and resinous substances, hydro- and oxycellulose, lignins, and bleach residues. Vegetable wax and resins and intercellular matter interfere with the successful nitration of the cellulose by the present rapid processes of nitration, due to the fact that the absorption of the nitrating acids is retarded and the uniformity of the nitration is interfered with. The physical condition of the cellulose also exerts an influence upon the resulting nitrocellulose as well as upon the success of the process of nitration.

H. Schwarz has described[1] experiments made in Germany on the use of wood cellulose which showed that conifer woods, containing on the average 0.4% to 0.5% of ash and about 8% to 10% of water, are the most suitable for this purpose, while soft woods, such as poplar and beech, yield inferior products. In preparing the wood the outer bark, dirt, etc., are removed, and the wood cut into sections about 1 m. long and 5 cm. thick, and these are shredded, while the harder parts (knots) are ground in a mill. The soda process gives a product which dissolves to some extent in the subsequent acid treatment, and is difficult to bleach, but, apart from the lower yield, the cellulose obtained by this process does not differ materially from that obtained by the sulfite-cellulose process.

The Ritter-Kellner method of direct boiling proved cheaper and yielded a cellulose which was softer and absorbed acid more readily than the product obtained by the Mitscherlich sulfite process. It was specified that suitable wood cellulose should weigh from 18 to 22 gm. per sq. m., should be in flocks of 5 to 10 cm. in size, free from small particles, dust, knots, and vegetable impurities. It should absorb acids readily (35 to 40 mins. per charge), and should be white and free from bleaching agent (chlorine).

The permissible limit for ash was fixed at 0.6%; fat and rosin, 0.5%; water, 6%; and wood gum (alkali-soluble constituent of cellulose), 2.5%. When nitrated it should not become pasty, and must not become more than pale yellow (not brown). It should be free from lignin. Cellulose and cellulose wool intended for

---

[1] Oesterr. Chem. Ztg. 1919, **22**, 50, 57; abst. J. S. C. I. 1919, **38**, 602-A.

the manufacture of smokeless powder must have been made from well-seasoned wood and be free from knots. After boiling and washing the unbleached cellulose should give, at most, a slight rose coloration in the phloroglucinol test. It should be bleached in the cold with a not too concentrated solution, washed, and dried at a temperature not exceeding 110°–120°. In 1915–1916 cellulose wool was only used as a partial substitute for cotton wool, but subsequently it was used alone.

Nitrated wood cellulose is usually chemically purer than cotton cellulose. It consumes somewhat less acid in nitration, and there is less risk of ignition. The opening of the compressed balls in the powder factory is more readily effected, and with less loss (dust) than in the case of the cotton product. It is also dried more rapidly, and there is less loss in washing the nitrocellulose, while the last traces of absorbed acid are removed more easily. On the other hand, wood cellulose is more voluminous than cotton cellulose, so that the nitration charge is reduced by about 10%. The adherent (as distinguished from the absorbed) acid requires longer washing to remove, and the absorptive capacity for acid is less than with cotton cellulose. On the whole, according to Schwartz, the advantages outweigh the disadvantages.

Nitrated wood pulp forms a separate topic in this volume called "Nitro-lignin," where are described the various methods for nitration of lignocellulose and the industrial applications of the nitrated lignocelluloses.

According to the patented process of W. Stevenson,[1] bleached sulfite wood pulp is used as the cellulose basis in the manufacture of acetylcellulose. A mixture of sulfite cellulose, 1 part; glacial acetic acid, 2.8; acetic anhydride, 4.0, and zinc chloride, 0.2 part, is digested at 60°–70° C. for 7–8 hours.[2]

In the writer's hands, acetated lignin is not a satisfactory product for the replacement of acetated tissue paper for aeroplane dopes, or more especially for the uninflammable continuous

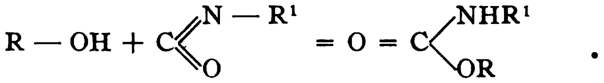
---

[1] E. P. 130029, 1917; abst. J. S. C. I. 1919, **38**, 714-A.

[2] According to the patent specification, zinc chloride is employed as catalyst, the acetylating bath being composed of, 1 k. bleached sulfite paper pulp, 2.8 k. glacial acetic acid, 4. k. acetic anhydride (strength not stated), and 200 gm. zinc chloride. These are thoroughly mixed and allowed to stand at 60°–70°. "I thus obtain my precipitate, which is thoroughly washed and dried in a temperature of 100°–120°. The precipitate is easily dissolved in pure acetone to form a transparent solution."

photographic films. In tensile strength, tenuity and viscosity of solutions it is decidedly inferior to acetated filter paper. The clarity and solubility of acetated lignocellulose is satisfactory. The acetated celluloses are described in Volume VIII of this series.

Cellulose Carbamates. Recently there has been brought to the attention of chemists an apparently new class of cellulose derivatives. For some time it has been known that alcohols and phenols act upon the aliphatic or aromatic isocyanates, thereby producing esters of the alkyl- or aryl-carbamic acids.



$$R - OH + C\begin{matrix} /\!\!/ N - R^1 \\ \diagdown O \end{matrix} = O = C\begin{matrix} \diagup NHR^1 \\ \diagdown OR \end{matrix} .$$

P. Goissedet[1] has found that this reaction can be applied to cellulose and to its derivatives containing hydroxyl radicals. When, for instance, phenyl isocyanate is allowed to act upon cellulose in the presence of tertiary bases the cellulose is transformed into phenyl carbamic esters, which the patentee claims can be applied to the same uses as the cellulose esters.

This product may be prepared by heating together one part of dried cotton with 3 parts of phenyl isocyanate diluted with dry pyridine, the amount of pyridine employed being about 6 times the weight of the cellulose used. The mass is stirred at about 120° for from 12 to 24 hours, during which time the cotton fibers gradually disappear leaving a colloidal solution from which the insoluble cellulose phenyl carbamic ester is precipitated by water. At the same time small amounts of diphenyl urea are formed which are separated from the ester by a solvent for the diphenyl urea, as petroleum ether.

The ratio of pyridine to cellulose may vary within comparatively wide limits. The former apparently aids in the reaction in addition to acting as a desirable diluent. Due to the fact that the process may be carried out in the presence of tertiary bases either singly or intermixed, products may be obtained having a wide range of solubility in the usual cellulose ester solvents. In general, the longer the esterifying materials are allowed to act upon the cellulose, the greater is the solubility in a given solvent or solvent mixture.

Cellulose derivatives of sulfinic acid have been described by

---

[1] E. P. 130277, 1919.

Knoll & Co.[1] and are obtained by bringing cellulose, hydrocellulose or oxycellulose in contact with sulfinic acid and organic anhydrides. In the presence of the necessary amounts of suitable solvents, the cellulose goes into solution in the form either of sulfur-contained or sulfur-free cellulose derivatives.

Animal Celluloses. Compounds of the aggregate composition of cotton cellulose have been described, resulting from the isolation of certain bodies from the mantle of Ascidia and other invertebrates by extended hydrolytic treatment. Such residues have been investigated by C. Schmidt,[2] M. Berthelot,[3] Schaefer,[4] C. Loewig and A. Koelliker,[5] and A. Franchimont,[6] from which

---

1. D. R. P. 180666, 1905; abst. Chem. Centr. 1907, **78**, I, 773.

2. Ann. 1845, **54**, 318; J. prakt. Chem. 1846, **38**, 433. This product was discovered by Schmidt in 1846, and distinguished from cellulose and named "tunicin" by Berthelot.

3. Compt. rend. 1858, **47**, 227; Ann. Chim. Phys. 1859, **56**, 149; Rep. Chim. Pure, 1859, **1**, 69; J. prakt. Chem. 1859, **76**, 371; Pharm. Centr. 1858, **29**, 675. M. Berthelot and G. Andre, Compt. rend. 1890, **110**, 925; abst. Chem. News, 1890, **61**, 253; J. C. S. 1890, **58**, 937; Bull. Soc. Chim. 1890, **4**, 230; Jahr. Chem. 1890, **43**, 284. See also R. Schütze, Mitth. pharm. Inst. Erlangen, 1889, **2**, 280; abst. Chem. Centr. 1889, **60**, II, 588; Jahr. Tierchem. **19**, 328. A. Franchimont, Compt. rend. 1879, **89**, 711, 713, 755; Ber. 1879, **12**, 1938; abst. Chem. News, 1879, **40**, 264; J. C. S. 1880, **38**, 233; Jahr. Chem. 1879, **32**, 832; Fuerth, Vergl. Chem. Physiol. d. nied. Tiere, 1903, 467.

4. Ann. 1871, **160**, 312; abst. Chem. News, 1872, **25**, 107; J. C. S. 1872, **25**, 309; Bull. Soc. Chim. 1872, **17**, 371; Jahr. Chem. 1871, **24**, 789. See Dumas, Edwards, Boussingault and Payen, Compt. rend. 1846, **22**, 581; Ann. Sci. nat. 1846, 238. Schlossberger, J. prakt. Chem. 1858, **73**, 374.

5. J. prakt. Chem. 1846, **37**, 439; Compt. rend. 1846, **22**, 38; abst. Annuaire de Chim. 1847, **3**, 694; Ann. Sci. nat. (3), **5**, 193; Berz. Jahr. Chem. 1848, **27**, 685. E. Schulze, Zts. physiol. Chem. 1892, **16**, 387, 427; abst. J. C. S. 1892, **62**, 907; J. S. C. I. 1892, **11**, 49; Bull. Soc. Chim. 1892, **8**, 491; Ber. 1892, **25**, R, 434; Chem. Centr. 1892, **63**, I, 700; Chem. Ztg. Rep. 1892, **16**, 215; Jahr. Chem. 1891, **44**, 2208; 1892, **45**, 2138; Ber. 1891, **24**, 2277; abst. Chem. Centr. 1891, **62**, II, 472. R. Gans and B. Tollens, Ann. 1888, **249**, 218; abst. J. S. C. I. 1888, **7**, 595; Bull. Soc. Chim. 1889, **1**, 746; Ber. 1888, **21**, 2148; Chem. Tech. Rep. 1888, **27**, II, 289; Jahr. Chem. 1888, **41**, 2309; Wag. Jahr. 1888, **34**, 954. E. Winterstein, Ber. 1893, **26**, 362; Zts. physiol. Chem. **18**, 43; abst. J. C. S. 1893, **64**, 380, 497; J. S. C. I. 1893, **12**, 702; Bull. Soc. Chim. 1893, **10**, 699; Chem. Centr. 1893, **64**, I, 602, II, 218; Jahr. Chem. 1893, **46**, 880; Meyer Jahr. Chem. 1893, **3**, 236; Jahr. Tierchem. 1893, **23**, 57.

6. Compt. rend. 1879, **89**, 711, 713, 755; abst. Ber. 1879, **12**, 1938; Chem. News, 1879, **40**, 264; J. C. S. 1880, **38**, 233; Jahr. Chem. 1879, **32**, 832; Jahr. Tierchem. 1879, **9**, 52. W. Stone and B. Tollens, Ann. 1888, **249**, 259; abst. J. C. S. 1889, **56**, 480; J. S. C. I. 1888, **7**, 511; Ber. 1888, **21**, 1572; Jahr. Chem. 1888, **41**, 2459. F. Hoppe-Seyler, Ber. 1894, **27**, 3329; abst. J. C. S. 1895, **68**, i, 166; Bull. Soc. Chim. 1895, **14**, 765; Chem. Centr. 1895, **66**, I, 393; Jahr. Chem. 1894, **47**, 1131; Meyer Jahr. Chem. 1894, **4**, 289; Jahr. organ. Chem. 1894, **2**, 894. E. Salkowski, Ber. 1894, **27**, 497, 925, 3325; abst. J. C. S. 1894, **66**, i, 222; 1895, **68**, i, 166; J. S. C. I. 1894, **13**, 411; 1895, **14**, 376; Bull. Soc. Chim. 1894, **12**, 1051; 1895, **14**, 698; Chem. Centr. 1894, **65**, I, 624; 1895, **66**, I, 328; Jahr. Chem. 1894, **47**, 2344; Meyer Jahr. Chem. 1894, **4**, 288; Jahr. organ. Chem. 1894, **2**, 221.

it appears that the sugar obtained as the product of hydrolysis is similar to or identical with the dextrose obtained from certain vegetable celluloses. Cellulose has also been identified as a constituent of œmeba and other protozoa, the investigations of W. Halliburton[1] on the investing membrane of Ophrydium versatile indicating such matrix to consist primarily of a cellulose similar to those of the tunicates. R. Virchow[2] also found cellulose in degenerated human spleen.

As E. Abderhalden and G. Zemplen have emphasized[3] that the mere obtaining of dextrose from tunicin and similar animal bodies does not necessarily establish its identity with vegetable cellulose. Further proofs of the identity or close relationship have been adduced by these investigators, who have found that, (1) by the action of acetic anhydride in the presence of sulfuric acid an acetyl compound (octacetylcellobiose) was obtained, with the same melting point, solubility, composition, and optical activity as the product similarly obtained from filter paper; (2) the osazones of the cellobiose are also identical, (3) by saponification

---

1. Quart. J. Micr. Sci. 1885, **25,** 173, 445; abst. J. Roy. Micr. Soc. 1885, **5,** 222.

2. Compt. rend. 1853, **37,** 492, 860; abst. Pharm. Centr. 1853, **24,** 768; Jahr. Chem. 1853, **6,** 592; J. prakt. Chem. 1854, **61,** 59. Cellulose does (Peligot, Compt. rend. 1858, **47,** 1037; Ann. Chim. phys. 1860, (3), **58,** 83; abst. Rep. Chim. Pure, 1859, **1,** 234; Chem. Centr. 1860, **31,** 341; Jahr. Chem. 1858, **11,** 574) not (G. Staedeler, Ann. 1859, **111,** 28; abst. Rep. Chim. Pure, 1859, **1,** 569; J. Pharm. (3), **36,** 229; Chem. Centr. 1859, **30,** 705; Jahr. Chem. 1859, **12,** 598; J. prakt. Chem. 1859, **78,** 169) occur in the skin of silk worms; and does (H. Ambronn, Mitt. zool. Station Neapl. 1890, **9,** 475; abst. Jahr. Tierchem. **20,** 318; J. Roy. Micro. Soc. 1890, 704) not (F. Schulz, Zts. physiol. Chem. 1900, **9,** 475; abst. J. C. S. 1900, **78,** ii, 292; Bull. Soc. Chim. 1901, **26,** 32; Chem. Centr. 1900, **71,** I, 729; see also Krawkow, Zts. Biol. **11,** 177; Zander, Pflüger's Archiv. **66,** 545) occur in the shield of Os sepia.

3. Zts. physiol. Chem. 1911, **72,** 58; abst. J. C. S. 1911, **100,** i, 525; C. A. 1912, **5,** 3081; Bull. Soc. Chim. 1912, **12,** 524; Chem. Zentr. 1911, **82,** II, 625; Meyer Jahr. Chem. 1911, **21,** 264.

For the constituents of the tissues of fungi, refer to E. Winterstein, Zts. physiol. Chem. 1894, **19,** 521; 1895, **21,** 134. E. Schulze, Ibid. 1894, **18,** 711. R. Reiss, Landw. Jahr. **18,** 711. Braconnot, Jour. de physique, 1811, 73. Payen, Ann. Sci. nat. (2), **2,** 21. A. Doepping, Ann. 1844, **52,** 106. C. Richter, Sitzungsber. Akad. Wiss., Wien, **83,** I, 494. Fueisting, Botan. Ztg. 1868, 661. W. Hoffmeister, Landw. Jahr. 1888, 239. J. Schlossberger, Ann. 1844, **51,** 207. Naegeli and Loew, J. prakt. Chem. 1878, **125,** 403. A. Brown, J. C. S. 1886, **49,** 432; 1887, **51,** 643; Ber. 1886, **19,** R, 463. E. Gilson, Ber. botan. Ges. **11,** 441; Compt. rend. 1895, **120,** 1000. J. Dreyfus, Zts. physiol. Chem. 1894, **18,** 358. V. Fleschig, Zts. Physiol. Chem. **7,** 525. L. Mangin, Compt. rend. 1893, **118,** 816. T. Araki, Zts. physiol. Chem. 1895, **20,** 504.

of the acetyl compound by means of barium hydroxide in the cold, crystallized cellobiose was obtained.

So far as aware, no attempts have been made to esterify these bodies into the corresponding nitrates and acetates.

Esparto. Esparto grass, *Stipa, macrochloa* (*tenacissima*), grows wild in Spain, Portugal, Greece, and various districts in Northern Africa, especially in the Algerian area.[1] It grows readily on sandy ferruginous soils and large crops are obtained without artificial cultivation. The grass attains a height of three to four feet, has a narrow cylindrical stem coated with stout hairs, the haulms being 0.3 to 0.5 mm. long and 1 to 1.5 mm. thick. The bast fibers are grouped together. The cuticular and bast fibers examined microscopically are seen as narrow cylinders with pointed ends. The Spanish type of esparto is considered one of the best for cellulose production. Other types employed for paper making, etc., are known by the terms: Northern African, Oran, Tunis, Arzen, Gabes and Sfax. A grass known as: Tripoli esparto (*Imperata cylindrica* P. B.) is very similar to esparto, and gives a 40% yield of cellulose.[2]

The grass is pulled during dry summer weather, tied into bundles and packed by hydraulic presses into bales for export. Before conversion into pulp, the grass is subjected to a mechanical purification. The bales are opened and the loose fibers having been cut up into suitable lengths, are spread on wire netting supported in frames. Impurities, such as clay or sand, pass through the sieves. The grass is also hand-picked and other foreign matter removed, this stage of the process being known as "dry picking."[3] The preliminary cleaning is readily carried out also by the aid of machinery in which the crude fiber is agitated.

The cuticle of esparto grass contains a wax of industrial importance.[4] In the process of dusting of the grass prior to its conversion into paper pulp, a portion of this cuticular wax is mechanically removed, another portion being recovered during the

---

[1] E. Goulding and W. Dunstan, "Cotton and Other Vegetable Fibers," 219.

[2] F. Vignolo-Lutati, L'Ind. Chim. 1913, 13, 17; abst. J. S. C. I. 1913, **32**, 228; C. A. 1913, **7**, 3413.

[3] Thorpe, Dictionary Applied Chemistry, article "Esparto," 2, p. 348.

[4] C. Cross and D. Russell, F. P. 395250, 1908; E. P. 8268, 1908; abst. J. S. C. I. 1909, **28**, 372; C. A. 1909, **3**, 2392.

subsequent chemical treatment to which the material is exposed.

The grass is next heated with caustic soda at a pressure of 10–50 lbs. for five hours, the amount of caustic soda required being approximately one-quarter of the weight of esparto treated. After removal of mother liquor and thorough washing of the residual cellulose fiber, the latter is again spread out and hand picked (wet picking) to remove any portions which have been incompletely boiled. In the newer press-pâte system the bleached pulp is passed through a series of strainers or knotters. The subsequent working up of the cellulose pulp from esparto is similar to that described under jute or wood pulp.

With modifications in the alkali treatment, various materials in addition to esparto may be utilized in the preparation of cellulose pulp.[1] Among the materials which have been so employed are plants generally,[2] the fiber of *Ulex europens* (ajonc),[3] rhea,[4] ramie,[5,6] gorse,[7] hemp,[8] hop runners,[9] corn stalks,[10] corn pith,[11]

1. O. Silberrad, F. P. 434709, 1911; abst. J. S. C. I. 1912, **31**, 279. E. P. 28193, 1910; abst. J. S. C. I. 1912, **31**, 67; C. A. 1912, **6**, 1534.
2. C. Kellner, E. P. 24542, 1902. F. P. 326313, 1902; abst. J. S. C. I. 1903, **22**, 817, 1145. For comprehensive analyses of fibers, consult Bull. Imp. Inst. 1917, **15**, 7; abst. C. A. 1917, **11**, 3443; J. S. C. I. 1917, **36**, 1003.
3. G. Horteloup, E. P. 26149, 26150, 1903; 21505, 1905; abst. J. S. C. I. 1904, **23**, 266, 500; 1906, **25**, 441. F. P. 327136, 1902; 331176, 1903; 347353, 1904; abst. J. S. C. I. 1903, **22**, 879, 1145; 1905, **24**, 344; Mon. Sci. 1903, **59**, 195. He proposed to nitrate the cellulose from Ulex Europens for the manufacture of artificial silk, celluloid and guncotton. H. Davoine (F. P. 470606, 1914; abst. J. S. C. I. 1914, **33**, 172) advocated the nitration of Hedychium coronarium for the same purpose.
4. W. Cordner, E. P. 13846, 1899; abst. J. S. C. I. 1900, **19**, 734; Kunst. 1913, **3**, 390; U. S. P. 654691, 654951, 654952, 1900.
5. J. Rossi, Manchester Guardian, May 7, 1919; abst. J. S. C. I. 1919, **38**, 188-R.
6. P. Birkenstock, U. S. P. 949643, 1910; 1004974, 1911; abst. C. A. 1910, **4**, 1106; 1912, **6**, 300. F. P. 404037, abst. Mon. Sci. 1911, **75**, 154; F. P. 434416, 1911; abst. J. S. C. I. 1912, **31**, 328. He purified the material by first boiling in sodium sulforicinate and NaOH, washing, then steeping in dilute mineral acid, and finally bleaching.
7. A. Bouret and A. Verbrese, E. P. 24768, 1898; abst. J. S. C. I. 1900, **19**, 42. For data on cocoanut fiber, see H. Matthes, Ber. 1908, **41**, 400; abst. J. C. S. 1908, **94**, ii, 236. H. Matthes and F. Streitberger, Ber. 1907, **40**, 4195; abst. J. C. S. 1907, **92**, ii, 991. H. Matthes and Muller, Zts. Nahr. Genussm. 1906, **12**, 159. J. Koenig, Ber. 1908, **41**, 46. J. Torrilhon, U. S. P. 496075, 1893. F. P. 196095, 1889.
8. C. Hengst, E. P. 13656, 1888; abst. J. S. C. I. 1889, **8**, 478; 1890, **9**, 325; Wag. Jahr. 1890, **36**, 546; Zts. ang. Chem. 1890, **3**, 247; Tech. Chem. Jahr. 1889, **12**, 165; Chem. Tech. Rep. 1890, **29**, I, 222; Chem. Ztg. 1890, **14**, 408; Jahr. Chem. 1890, **43**, 271; Proc. U. S. Nav. Inst. 1889, **15**, 497. Paper Maker, 1919, **57**, 152; J. Ind. Eng. Chem. 1919, **11**, 479; C. A. 1919,

vegetable pith such as from corn stalks, waste vegetable fiber,[1] sugar cane megass,[2,3,4] straw,[5] flax straw, bamboo,[6] and cocoanut

13, 1390. R. Sherwood, U. S. P. 40577, 1863. G. Sellers, U. S. P. 40576, 1863. W. Woodbridge, U. S. P. 39981, 1863.

9. C. Muller and D. Wolf, F. P. 443133; E. P. 5659, 1912; abst. J. S. C. I. 1912, **31,** 1029; 1913, **32,** 133. D. R. P. 256351; abst. C. A. 1913, **7,** 1982; Wag. Jahr. 1913, **59,** II, 442; Chem. Zentr. 1913, **84,** I, 867; Chem. Ztg. Rep. 1913, **37,** 116; Zts. ang. Chem. 1913, **26,** 175. The bast sheath or fibrous material surrounding the pith of hop runners is separated from the woody and other matter with which it is associated, being then boiled in sodium carbonate and soft soap with an addition of caustic soda up to 5%. By this process the bast sheath is loosened from the ligneous portion and can readily be separated by peeling. The fibrous raw material thus obtained is then bleached, washed and dried, when it is in condition for nitration. According to the patentee "the product thus obtained is ready for direct use" for filament formation, and "artificial silk thus produced has a flexibility hitherto possessed only by natural silk, and textile goods made of this fiber cannot be distinguished from pure silk."

10. Sci. Amer. 1905, **92,** 505. For making yarn from kapok fiber, see J. de Saint-Rene and J. Tissier, E. P. 27303, 1910.

11. Engineering, **83,** 9. Consult the topic, "Nitrates of the Carbohydrates."

1. I. Herz, U. S. P. 1041791, 1912; abst. C. A. 1912, **6,** 3518; J. S. C. I. 1912, **31,** 1075; E. P. 23255, 1911; 19334, 1912; abst. J. S. C. I. 1912, **31,** 1176; F. P. 422490, 1910; abst. J. S. C. I. 1911, **30,** 533.

2. R. Lhuilier and L. Maurice, F. P. 405684, 1909; abst. J. S. C. I. 1910, **29,** 417; Mon. Sci. 1911, **75,** 148. The cellulosic material is preferably packed in iron baskets which can be immersed in boilers, lifted out and transferred to other boilers without unloading. The chemical treatments consist of a digestion, at the boiling temperature or otherwise, in a solution of an alkali carbonate, followed by a bleaching operation by means of an alkaline solution of an alkali hypochlorite. The digestion with sodium carbonate is best effected with a "battery" of three boilers in order to obtain a systematic exhaustion of the liquors.

3. V. Drewsen, U. S. P. 853943, 1907; abst. J. S. C. I. 1907, **26,** 713; C. A. 1907, **1,** 2191.

4. V. Drewsen, U. S. P. 731290, 1903; 789416, 1905; abst. J. S. C. I. 1903, **22,** 876; 1905, **24,** 633.

5. E. Heuser and A. Haug, Zts. ang. Chem. 1918, **31,** 166; abst. J. S. C. I. 1918, **37,** 365-A, 650-A; C. A. 1918, **12,** 2439. In their process the crude cellulose prepared by the chlorination method with the use of caustic soda contained only 0.35% of ash, whereas that prepared with the use of sodium sulfite contained 1.1%. The yield was 54.60% of crude cellulose with furfural value 13.30%, equivalent to 22.34% of xylan. Hence the calculated yield of true cellulose was 42.97%. The original straw had furfural value 15.4, equivalent to 25.62% of xylan on the dry and ash-free basis; thus 47.32% of the original xylan remained in the cellulose. The proportion of xylan remaining in the cellulose varies inversely as the yield of cellulose and is a function of the concentration of the caustic soda solution used for extracting the chlorinated products. For instance, the furfural value of 13.3 was found when a 1% solution of caustic soda was employed; with a 2% solution the furfural value of the crude cellulose fell to 10.4, and with a 3% solution to 9.3. The furfural value of commercial straw cellulose also varies with the yield and with the severity of the chemical treatment; it may reach 18%. Most of the xylan may be removed from the crude straw cellulose preparations by repeated extraction with 6% caustic soda solution, but it has not been found

shell,[1] all of which have been nitrated and whose nitric esters are described in Part III of this volume.

T. Knösel, in the preparation of cellulose from vegetable fibers replaces 25% of the caustic soda in the soda boil by sodium carbonate, and largely dilutes the lye so that it amounts to 5–10 times the weight of the fiber. The boiling is carried out at atmospheric pressure for four hours, the separated material next bleached using two-thirds the amount of the bleaching material employed in the ordinary process and the washed fiber again boiled with alkali. In this latter case the boiling solution only

---

possible to reduce the furfural value of the cellulose below 1.95% in this manner. Attempts to remove the whole of the xylan by extraction before chlorination as well as afterwards, led to a similar result, and a fully extracted preparation from commercial bleached straw pulp still gave 2.02% of furfural. Commercial bleached straw cellulose shows a "copper value" of 3.0; unbleached straw cellulose, on the other hand, has a "copper value" of 0.94–0.99, and bleached straw cellulose which has been fully extracted until the furfural value is reduced to the limit of 2.0% shows a "copper value" of only 0.61–0.78. Moreover, by further bleaching and the production of oxycellulose, the "copper value' of this product may be increased to 15.5 without any effect on its furfural value. Hence it is concluded that straw cellulose does not correspond to a special type of "natural oxycellulose," but is an ordinary cellulose similar to that of cotton or wood, strongly contaminated with a pentosan and modified by bleaching under industrial conditions in such a way that the commercial pulp contains a substantial amount of oxycellulose. The only outstanding question is the nature of the residual 2% of furfural which cannot be eliminated by extraction of the purified cellulose. On hydrolysis with 1% sulfuric acid at 135° for half an hour, this furfural-yielding residue is divided half in the hydrolyzed liquid and half in the hydrocellulose. An examination of the liquid and the preparation of the benzoate and osazone, m. pt. 160°–180° C., suggested the presence of xylose, and it is probable that the residue in question consists merely of a trace of xylan, equivalent to less than 1% of furfural, which is obstinately retained by the cellulose, while 1.0–1.5% of furfural may be attributed to the cellulose itself, just as in the case of cotton cellulose. Hydrolysis with 72% sulfuric acid followed by digestion of the diluted liquid at 120° C. for 2 hours, according to the method of Ost and Wilkening, was carried out on the purified straw cellulose. The results were compared with those obtained with pure dextrose, observations being made of cupric-reducing power, polarization, yield of alcohol by fermentation, and the m. pt. of the osazone. These were all in close agreement and afforded satisfactory evidence that the resolution of straw cellulose to dextrose is practically complete and that its constitution corresponds with that of cotton cellulose. A. Lyman, U. S. P. 40696, 1863. A. Tait, U. S. P. 40728, 1863.

[6] T. Knösel, F. P. 435895, 1911; abst. J. S. C. I. 1912, **31**, 381. D. R. P. 252411, 1910; abst. Wag. Jahr. 1912, **59**, II, 549; Chem. Zentr. 1912, **83**, II, 1710; Chem. Ztg. Rep. 1912, **36**, 610; Zts. ang. Chem. 1912, **27**, 2384; C. A. 1913, **7**, 416.

[1] Germain, F. P. 192181, 1888; abst. Mon. Sci. 1889, **33**, 507. Used as an explosive after treatment. Cf. J. Dypowski and Societe Textile du Centre, F. P. 486323; abst. C. A. 1919, **13**, 1936. C. Schwalbe, D. R. P. 309555, 1917; abst. J. S. C. I. 1919, **38**, 295-A.

contains 0.5%–1.0% of sodium carbonate. In a recent French patent[1] a method is described for the production of cellulose from various types of fibrous materials. The chemical treatment consists in boiling with alkali carbonate followed by a bleaching operation by means of alkali hypochlorite solution. The alkali digestion is carried out in a battery of 3 boilers in order to obtain a systematic exhaustion of the liquors.

It has also been suggested to replace the soda by ammonia.[2] The fiber is boiled under pressure in an alkali solution containing ammonia, animal fat and soap, washed and subsequently treated with a boiling solution containing in addition, vegetable oil, oleic acid and boric acid or a borax compound.

According to a method patented in France,[3] vegetable fibers may be converted into cellulose as follows: The cleaned material is submitted to a preliminary drying in order to render the cellulose more resistant in the subsequent treatment, after which the fibers are placed in a tank with a false bottom formed of an iron grid which acts as a positive electrode. Sufficient water (slightly acid) is placed in the tank to cover the fiber. A negative electrode is fixed in the upper portion of the tank in contact with the water, through which a current of 0.5 ampere at 2 volts is passed, and this, it is claimed, accelerates the action of the pectase on the pectoses present, these later being converted into soluble compounds. The current is then turned off and the material treated with dilute alkali (0.5 kilos of alkali per 100 kilos of fiber), the liquid meanwhile being agitated by air. By this method of treatment the fatty and resinous matter and the chlorophyll are removed. The cellulose is next bleached and washed with alkali and finally with water. The residue consists of a pure cellulose quite suitable for paper manufacture. Cellulose may also be obtained from various vegetable materials such as maize stems, by first removing the water-soluble constituents and then treating the moist material with nitric oxide and steam. An alternative

---

[1] L. Dewolf-Wante, F. P. 458289, 1913; abst. J. S. C. I. 1913, **32**, 1063. Holl. P. 1538, 1916; abst. C. A. 1916, **10**, 3167. Societe Darrasse Freres and L. Dupont, E. P. 123326, 1919; abst. C. A. 1919, **13**, 1478. A. Angell, U. S. P. 219668, 1879.

[2] R. Roberts, U. S. P. 1062187, 1913; abst. J. S. C. I. 1913, **32**, 653; C. A. 1913, **7**, 2476; Can. P. 150728, 1913; abst. C. A. 1913, **7**, 4079.

[3] C. Tanquerel, F. P. 383099, 1907; abst. J. S. C. I. 1908, **27**, 352; Mon. Sci. 1908, **69**, 166; C. A. 1909, **3**, 1093.

process consists in treatment with a mixture of nitric oxide and chlorine. The purified fiber is washed, neutralized and again washed.[1]

The sulfite process is not directly applicable to esparto or material such as straw, on account of the silica present. The latter, it is claimed,[2] hindering the penetration of the liquor into the fiber. Silica, however, may be removed by treating the crude material for several hours with a 1.5% solution of hydrofluoric acid. The cellulose material after this treatment is washed with water until free from acid, and heated with 4–5 times its weight of liquor (containing 3.5% available sulfur dioxide). The yield of cellulose from straw will average about 42%.

On boiling with solution of aniline salts, esparto cellulose develops a rose color. It furthermore reacts with Fehling's solution, salts of phenylhydrazine, and magenta sulfurous acid solution, indicating the presence of active CO groups.[3] The fiber is slowly oxidized by dry air at 100°, becoming discolored in the process. With iodine dissolved in potassium iodide, a greyish brown color is obtained, while with zinc chloride and iodide a bluish violet stain is produced.

The carbon percentage of esparto cellulose varies from 41–42.4 and the hydrogen content from 5.4–5.8. An exception to this is recorded by C. Cross and E. Bevan for a particular esparto cellulose which gave the following results: Carbon 44.68%, hydrogen 6.16%.[4] the yield of furfural being 12.5%. From these

---

[1] F. Stewart, U. S. P. 845378, 1907; abst. J. S. C. I. 1907, **26**, 548; C. A. 1907, **1**, 1071. See U. S. P. 811523, 1906; abst. J. S. C. I. 1906, **25**, 226. Cellulose is obtained from the stems of maize and similar plants by removing the water-soluble constituents, leaving the stalks in a divided and absorptive condition, and then treating the material when moist, either with nitric oxide and steam, or with a mixture of nitric oxide and chlorine, subsequently washing, neutralizing, and again washing the cellulose.

[2] R. Dietz, Zts. ang. Chem. 1905, **18**, 648; abst. Chem. Centr. 1905, **76**, I, 1676; J. S. C. I. 1905, **24**, 557; Jahr. Chem. 1905–1908, II, 971.

[3] Cross and Bevan, Cellulose, p. 84.

[4] C. Cross and E. Bevan, J. C. S. 1918, **113**, 182; abst. J. S. C. I. 1918, **37**, 236-A; C. A. 1918, **12**, 1380. They have recently (J. Soc. Dyers Col. 1919, **35**, 70; abst. J. S. C. I. 1919, **38**, 249-A) investigated raffia, a complex tissue composed of a true epidermis or cuticle and underlying sclerenchyma, the cells of which are sufficiently elongated to rank as fibers; under most chemical treatments the two tissues exhibit a joint resistance. The material showed: moisture, 8%–9%, ash 2.7%; on boiling with 1% caustic soda solution the loss was 16.8% in 5 minutes and 24.3% in 60 minutes. The attack by aqueous caustic soda was not, however, sufficiently specific to afford a pure preparation of cellulose by the chlorination method. On the

figures it appears that the composition of esparto cellulose corresponds to that of a normal cellulose containing 30% of furfuroid constituent. Esparto cellulose resembles oxycellulose rather than normal cellulose. Although it is generally assumed that the furfuroid grouping in esparto is of pentosan configuration, there is no direct proof that such is the case, and the experimental work of C. Cross and E. Bevan throw doubt on the accepted "furfuroid-pentose" relationship of esparto cellulose. They find that simple treatments so modify the constitution of the complex that the total yield of furfural is reduced to a large degree. Treatment at 15°–20° with 17.5% sodium hydroxide gives 84.14% of resistant cellulose with a furfural value of 4, and 15.86% of a hydrolyzed product with a furfural value of 26. The total furfural value is reduced from 12.5 to 7.48. With dilute sulfuric acid treatment a reduction in furfural value is also obtained. The fixation of SO_4 groups, according to C. Cross and E. Bevan, indicates the reactivity of oxygen of basic function in excess of that which

other hand, a preliminary treatment with alcoholic caustic soda broke down the resistance of the cutocellulose ester and subsequent chlorination yielded 42% of cellulose. The loss of weight with alcoholic soda was considerable: 39.94% with 2% NaOH and 46.7% with 5% NaOH. The residue after saponification was readily chlorinated, the lignone groups of the sclerenchyma fibers being attacked and the ultimate fibers, 2 mm. in length, being separated. The ratio of HCl formed to chlorine combined with the lignone was approximately 2:1. The isolated cellulose yielded 5.2% of furfural, as compared with 8% for the crude raffia. From the soaps of the alkaline hydrolysis, 11%–12% of a fatty acid and 6%–7% of a resin acid, the sodium salts of which are insoluble in alcohol, were separated. The fatty acid had a composition corresponding to the formula $C_{17}H_{32}O_3$, with one COOH and one OH group; iodine value (Wijs), 13.6%. The resin acid contained 58.4% of carbon and 10.0% of hydrogen. On fusion with aqueous sodium hydroxide at 250°–300° C. the separation of the fat constituent occurred with less modification, its lower acid value being held to indicate a higher molecular weight; the cellulose on the other hand, was profoundly decomposed with formation of volatile acids. Conversion into viscose, benzoylation and acetylation of the raffia gave mixed reactions of no sharply differentiated character. Nitration gave results indicating profound oxidation of the fat and resin components. The lignin reactions of raffia are considerably suppressed; it does not combine with phloroglucinol and reduces permanganate only to a limited extent. Certain effects of nitric acid are specific: a mixture of 36 parts of glacial acetic acid and 2 parts of nitric acid to 5 of raffia at 95° C. gave the fat-resin complex in solution in a form showing minimum modification. Dilute aqueous nitric acid produced a structural cleavage between the cuticle proper (40%) and the sclerenchymatous tissue (60%). The cuticle proper closely resembles that of apple peel. The general characteristics of raffia is that of an ester of fatty and resin acids with an oxidized modification of cellulose in intimate association with a lignocellulose ether. A purple reaction with ferric chloride, which is intensified by alkaline saponification, appears to be a characteristic of the complex tissue.

characterizes the alcoholic-hydroxyls of a hexose configuration.

Cellulose Filters. In addition to the ordinary filter paper, advantages of the use of cellulose as a filtering substance in sugar and other industries have been described by A. Aulard,[1] the advantages of wood pulp being that it is easily washed; gives a surface which is completely homogeneous as contrasted with the fibrous mesh of the cloth filter; the first liquid to come through a clean filter is as clear as the last; and varying thicknesses of pulp as needed for different liquids to be filtered may be easily adjusted. Data as to thicknesses of mat used and rapidity of filtration are given.

In the Prade system for the cellulose clarification of wines,[2] there is provided a closed cylindrical vessel inside of which are two concentric cylinders of filter-mass (cellulose) and held in place by perforated partitions. The whole is so arranged that the liquid filters through the inner and outer cellulose layers into the annular space between them.

An acid-resisting material intended more particularly for filtering gases containing acids in suspension, is prepared by heating cotton or similar fabric out of contact with air, to a temperature of from 200°–350° for from a few minutes to a week, according to the temperature employed. Cotton cloth weighing 350 gm. per square meter and having a tensile strength of 2300 kilos per meter, when heated to 300°–400° for periods of from 10 minutes to one hour, showed a loss of weight of from 68% to 76%, the tensile strength being reduced to 30–35 kilos per meter. The material retains its flexibility.[3]

Siemens and Halske[4] have described a diaphragm particularly suitable for use in chlorine-alkali electrolytic cells with horizontal electrodes, which is made from a mixture of powdered cement and cellulose, or material containing cellulose, mixed to a pulpy mass with water. The diaphragms thus produced are said to be strong and somewhat pliable, and to possess excellent porosity, the latter property being varied by the amount of con-

---

[1] Orig. Com. Eighth Intern. Cong. Appl. Chem. 1912, **25**, 489; abst. C. A. 1913, **7**, 3045.

[2] F. P. 319029, 1902; abst. J. S. C. I. 1903, **22**, 224.

[3] Metallbank & Metallurgische Ges., F. P. 456524, 1913; abst. J. S. C. I. 1913, **32**, 1094; C. A. 1914, **8**, 1860. D. R. P. 275662, 1913; abst. C. A. 1915, **9**, 133; Chem. Ztg. Rep. 1914, **38**, 418; Zts. ang. Chem. 1914, **27**, 539.

[4] D. R. P. 307471, 1916; abst. J. S. C. I. 1918, **37**, 741-A.

tained cellulose. They possess the advantage of cheapness over the Billiter asbestos diaphragms. M. Sussmann[1] has patented the use of a special cellulose powder to be used as an absorbent for the electrolyte of secondary batteries, made by comminuting filter paper, which is purified by successive boilings in dilute sulfuric acid, caustic potash and alcohol.

Cellulose Plastics and Aggregates. In the plastic composition of P. Defaucamberge,[2] cellulose is mixed with the natural latex of rubber in the presence of viscose. Thus the physical properties of elasticity, tenacity and non-conductivity for electricity found in Para rubber are enhanced and made more resistant by the presence of the cellulose.

Heat-insulation is produced by H. MacFarland and R. Shoemaker[3] by cooking the fibrous portions of *Zostera marina* in 2% NaOH solution, separating the soluble substances and treating the fibrous residue with sulfuric acid, using the gummy product thus formed as a binder for the cellulosic portion.

In the soft-soldering or coating of metals, the composition when made up in stick or paste form is squirted into tubes made of cellulose, as the latter leaves practically no residue on burning away.[4]

The W. Freeman cellulose plastic[5] composition is produced by hydrolyzing cellulose with an alkaline solution, drying it, mixing the dry fiber with magnesium oxide, and causing the whole to set by adding a solution of magnesium chloride. C. Ellis[6] produces a fibrous plastic composition by means of cellulose agglutinated together by the solids precipitated from acid sulfite-cellulose waste liquor. A. and M. Weiser[7] soften and mould

---

[1] E. P. 22053, 1893; abst. J. S. C. I. 1895, **14**, 370.

[2] U. S. P. 943658, 1909; Can. P. 121286, 1909; abst. Kunst. 1911, **1**, 216. The plastic mass of F. Ahrens (D. R. P. 216629; Pap. Ztg. 1909, **34**, 4008; Chem. Zentr. 1910, **81**, I, 71; Chem. Ztg. Rep. 1909, **33**, 664; Zts. ang. Chem. 1910, **23**, 144) is composed of cellulose made plastic by means of zinc chloride.

[3] U. S. P. 1146190; abst. C. A. 1915, **9**, 2432. See U. S. P. 1139305, 1915; abst. C. A. 1915, **9**, 1691.

[4] A. Rosenberg, E. P. 23300, 1912; abst. J. S. C. I. 1913, **32**, 1115.

[5] U. S. P. 1183446, 1916; abst. J. S. C. I. 1916, **35**, 734. Compare E. P. 17624, 1904; abst. J. S. C. I. 1905, **24**, 893.

[6] U. S. P. 1246806, 1917; abst. J. S. C. I. 1918, **37**, 53-A.

[7] Swiss P. 77143, 1918; abst. C. A. 1918, **12**, 2248; Kunst. 1918, **8**, 214. For the artificial sponge manufacturing process of P. Raabe, see Belg. P. 261288, 1913; abst. Kunst. 1914, **4**, 393.

cellulose without the addition of a binder by means of high pressure. The cellulose absorbent pad of J. Grant,[1] and the artificial leather composition of J. Hofmeier[2] are similar.

A. Hill[3] has devised a process for applying a cellulose to the fibers of a hydrated cellulose fabric, precipitating the cellulose, washing out the solvent, and then coating the fibers with a proteid in solution, as albumen. By this means, it is claimed, artificial leathers may be produced which may be printed upon as in calico printing.[4]

D. Hennequin[5] manufactures washers for bottle capsules and stoppers from a sheet of cellulose, to each side of which is cemented a layer of vegetable parchment, which is then varnished. "Artificial wool"[6] and "excelsior,"[7] prepared from cellulose, have also been described.

In a recent process,[8] plastic masses are described which may

1. E. P. 8499, 1913.
2. E. P. 12023, 1885.
3. U. S. P. 705244, 1902.
4. A cleansing compound for teeth has been patented by G. Richter and J. Wilowski (D. R. P. 236619, 1910; abst. Zts. ang. Chem. 1911, **24**, 1533; Chem. Zentr. 1911, II, 327; C. A. 1912, **6**, 11; Wag. Jahr. 1911, **57**, II, 143; Chem. Ztg. Rep. 1911, **35**, 390) made by dissolving acid halides in an indifferent viscous solution of cellulose, which solidifies upon exposure to the air. The acid halides then decompose, and dissolve the tartar on the teeth.
5. E. P. 7083, 1911. See A. Deiss and C. Fournier, Belg. P. 213988, 215784, 215985, 218996, 1909.
6. C. Villedieu, F. Lebert and A. Coumbray, F. P. 459406, 1912; abst. J. S. C. I. 1913, **32**, 1153; Kunst. 1914, **4**, 116. F. P. 17916, addition to F. P. 459406; abst. Kunst. 1914, **4**, 155.
7. A. Borzner, U. S. P. 1165062, 1915; abst. J. S. C. I. 1916, **35**, 250; Chem. Ztg. Rep. 1914, **38**, 241; Kunst. 1914, **4**, 194.
8. Naamlooze Venootschap Hollandsch Zijde Maatschappij, E. P. 4521, 1913; Belg. P. 256046, 1913; abst. Kunst. 1914, **4**, 77. In the manufacture of "simili" silk (J. Debourg, F. P. 427113, 1910; U. S. P. 1018650, 1912; abst. J. S. C. I. 1911, **30**, 1050; Chem. Ztg. Rep. 1912, **36**, 249), fibers, such as flax, hemp, ramie, nettle, are packed in shallow circular trays which are stacked one above the other in a cage. The cage is lowered into an autoclave which is heated by a perforated steam-coil passing around the outside of the cage and terminating in a vertical portion passing through holes in the center of the trays, up the axis of the autoclave. The fibers are first digested in a solution of sodium carbonate of about 0.5% concentration for two hours under a pressure of 2–3 atmospheres. The liquor is drained off and replaced by one containing, per 1000 liter of water: 108 kilos of slaked lime, 5.25 of sodium bisulfite, 5.5 of sal ammoniac, 0.56 of sodium peroxide and 5.75 of magnesium salt. The fibers are again heated for two hours, washed, acidified and washed. The treated fibers are carded, combed and spun according to their nature. For the "celloyarn" of A. Kube Co., see Svensk Papperstidning, 1918, 523; abst. C. A. 1919, **13**, 515. For "paper yarn" see World's Paper Trade Rev. **67**, No. 8, p. 8. For the simili silk of

be formed by means of employing certain carbohydrates which are completely soluble in albumen in the presence of ammonia, but which, after drying or precipitation of the mass with acid without further treatment, lose this capacity of dissolving in water. The patentees find that certain oxycelluloses satisfy these conditions, especially those which are produced by the action of dilute nitric acid on cellulose. Such oxycelluloses are said to be completely soluble in dilute ammonia, but become insoluble upon heating the solution to 60°–80°. Valuable plastics are said to be produced by combining such oxycelluloses with ammoniacal-soluble albuminous bodies (glutins and casein), to which pigments and filling materials may be added.[1]

Pergamyn, perhaps better known as grease-proof imitation parchment paper, is prepared from strong Mitscherlich sulfite wood pulp by beating it until it acquires a gelatinous consistency. H. Hofmann,[2] who has studied the formation of pergamyn under various conditions, finds that the original pulp and the pergamyn both yielded equal quantities of water-soluble constituents and both contained pentosans and methylpentosans upon hydrolysis. He also found that when sulfite wood pulp was heated in a drying oven it suffered a progressive chemical change, and that upon subsequent hydrolysis with acid it yielded increased quantities of sugar (xylose), proportional to the degree and duration of the heating. The degradation of the sulfite wood cellulose by heat was scarcely perceptible after heating for 4 hours at temperatures below 90°, but became definite and distinct at temperatures between 90° and 100°. Other pulps such as straw, raw wood, and rye, suffered no change at 100°.[3] Tests for determining the

---

G. Ragot, refer to Belg. P. 185671, 185672, 1905. For "celloyarn," consult A. Leinveber, Kunst. 1918, **8,** 234; E. P. 10530, 1902; F. P. 320529, 1902; abst. J. S. C. I. 1903, **22,** 25, 757. Textilose, Belg. P. 256019, 1913; abst. Kunst. 1914, **4,** 75.

[1] Vereinigte Koln Rottweiler Pulverfabriken, Belg. P. 129882, 1897, produce a dense cellulose by beating ordinary cellulose until it hydrates to a point where it becomes structureless, then eliminating the water, adding other ingredients and moulding the dried finished product.

[2] Inaugural Dissertation, Gottingen, 1906; Papier Ztg. 1906, **31,** 4190, 4331; abst. J. S. C. I. 1907, **26,** 110; Zts. ang. Chem. 1907, **20,** 746; Wochbl. Papierfabr. 1907, **38,** 1137; C. A. 1907, **1,** 485, 2179; Gew. Bl. Wuert. 1901, **53,** 348; World's Paper Tr. Rev. **69,** 78. Compare Poly. Centr. 1860, **26,** 56, 207, 911, 1199. E. P. 12023, 1885.

[3] For résumé of recent progress in the industrial applications of cellulose, see A. Klein, Papier Ztg. 1906, **31,** 4286; Woch. Papierfabr. **38,**

grease-proof properties of pergamyn have been described.[1]

Cellulith.[2] According to G. Springer, Brunswig's cellulith is produced by grinding wood pulp in a paper beater until an apparently homogeneous mass, free from every trace of wood fiber, is obtained. This pulp is then drained from the bulk of its moisture by allowing it to run into a vat provided with a bottom of metallic boards, where it is subsequently dried, either in the air or in rooms having a temperature of about 40°. The product contracts greatly and finally forms a solid mass of the hardness of horn, which is sold under the above name. The material is not waterproof.[3] It has a sp. gr. of about 1.5, is not inflammable, can be worked with tools like wood or horn, and is very resistant to oils, fats, alcohols and petroleum. It is said to be applicable as a substitute for horn or ebonite and to be used for buffing and polishing wheels.[4]

Bacterial Action on Cellulose Materials. It is a well known fact that when cotton is stored in a moist warm atmosphere it

---

1813; abst. C. A. 1907, **1**, 2492; Chem. Zentr. 1907, **78**, I, 381; Chem. Ztg. 1906, **30**, 1259; Zts. ang. Chem. 1907, **20**, 610. F. Beltzer, Rev. gén. chim. 1909, **13**, 20.

[1] C. Bartsch, Mitt. K. Materialpruef. 1915, **33**, 441; abst. J. S. C. I. 1916, **35**, 923; C. A. 1917, **11**, 1748; Chem. Zentr. 1916, **87**, I, 1279. See Vereinigte Köhn-Rottweiler Pulverfabriken, E. P. 18930, 1897.

[2] For "Cellulite," see Proc. Amer. Pharm. Assoc. 1900, **48**, 787. For Xylolith, consult A. Fraass, Belg. P. 234005, 1911. H. MacFarland and R. Jay (E. P. 8004, 1915; abst. C. A. 1916, **10**, 2970) convert the cellulose of eel grass into a structureless mass by acid and alkaline treatment, and this is compressed into sheets.

[3] D. R. P. 3181, 1878, waterproofing being increased by nitrating the vulcanized fiber. J. S. C. I. 1901, **20**, 602; Gummi Ztg. **15**, 329 (G. Springer). Neues Erfind. Erfahr, 1899, **26**, 125; Pharm. Centralh. 1900, **41**, 333; Cosmos, 1900, **42**, 384; La Nature, 1900, **28**, II, 119; U. S. Consular Report, No. 64, p. 461.

[4] In the process of the Vereinigte Koehn-Rottweiler Pulverfab. (E. P. 18930, 1897; abst. Chem. Ztg. 1899, **23**, 10; J. S. C. I. 1898, **17**, 65) is described a method of producing a hard, dense, horny material from fibrous cellulose without the use of mechanical pressure, a solvent or of a cementing material, in which ordinary cellulose either in the natural or purified state is taken and beaten in water until the fibrous structure of the cellulose has been entirely destroyed. After removal of a portion of the water by pressing until 60%–90% remains, the paste is moulded into any desired form and left to dry either in the open air or at a temperature of about 40°. In the process of drying, the cellulose condenses and shrinks up into a hard mass of 1. 4–1.5 sp. gr., and in this condition may be worked with tools. This "cellulith" can be used for imitation ivory, horn, wood or lapis. See H. Arledter, E. P. 16085, 1912; abst. C. A. 1914, **8**, 247; J. S. C. I. 1913, **22**, 865; E. P. 684, 1913; abst. J. S. C. I. 1913, **32**, 865. See E. P. 2018, 1910; abst. J. S. C. I. 1911, **30**, 205; C. A. 1911, **5**, 2947. E. P. 6677, 1914; abst. C. A. 1915, **9**, 2588; J. S. C. I. 1915, **34**, 793. D. R. P. 237474, 1910; abst. J. S. C. I. 1911, **30**, 1058; C. A. 1912, **6**, 1990; Chem. Ztg. Rep. 1911, **35**, 481.

often deteriorates. The fibers become brittle and a large amount of fine, dust-like cotton results. This material is unsuitable for the production of a stable nitrocellulose. It is also known that when moist jute is baled, the fiber may be damaged "heart damage." In extreme cases the fiber is completely disintegrated and under slight pressure, breaks down to a fine dust.[1] The cause of these changes with cotton and jute is bacterial. The fermentation set up is not necessarily due to impurities, since even cellulose in a pure form is capable of being attacked by bacteria when a suitable culture food is present. The subject of the action of bacteria will be considered from the aspect of attack on cellulose or cellulose material generally, rather than from the view of bacterial action on cotton solely.

The resolution of the cellulose complex into simpler molecules may be brought about not only by the usual chemical hydrolyzing and oxidizing agents, but also by bacterial action. E. Mitcherlich,[2] in 1850, observed the bacterial decomposition of crude potato cellulose. Hoppe-Seyler[3] found that Swedish filter paper in presence of river mud was changed completely into soluble or gaseous products. In 1886 he put forward the view that the cellulose is first changed by hydration into a fermentable carbohydrate and that this latter breaks down to carbon dioxide and methane.

$$C_6H_{10}O_5 + H_2O_2 = C_6H_{12}O_6 \longrightarrow 3CO_2 + 3CH_4.$$

The presence of hydrogen is assumed to be derived from acetic acid, which may be formed as an intermediate product. In the breaking down of the cellulose molecule by the aid of bacteria, no intermediate compounds have been isolated. The main products identified by V. Omelianski[4] are methane, hydrogen, carbon

[1] C. Cross and E. Bevan, Researches on Cellulose, III, 128.

[2] Ber. Berlin. Akad. 1850, 102; Ann. 1850, **75**, 305; J. prakt. Chem. 1850, **50**, 44; J. de Pharm. 1851, **19**, 145; Chem. Gaz. 1851, 61; Instit. 1850, 228; Jahr. Chem. 1850, **3**, 541; Pharm. Centr. 1850, **21**, 385.

[3] Zts. physiol. Chem. 1886, **10**, 200, 401; abst. J. C. S. 1886, **50**, 577, 932; Ber. 1886, **19**, 766, 879; Jahr. Chem. 1886, **39**, 1873; Wag. Jahr. 1886, **32**, 1036. For the estimation of hydrogen in methane, see Zts. physiol. Chem. 1887, **11**, 257; abst. Chem. Ind. 1887, **10**, 362; Chem. Tech. Rep. 1887, **26**, II, 257; Chem. Centr. 1887, **58**, 1166.

[4] Compt. rend. 1897, **125**, 970, 1131; abst. Jour. Chem. Soc. 1898, **74**, i, 291; J. S. C. I. 1898, **17**, 60, 171; 1900, **19**, 679; Bull. soc. chim. 1898, (3), **19**, 203, 204; Chem. Centr. 1898, **69**, I, 269; 1900, **71**, I, 918; Chem. Ztg. 1897, **21**, 1057; Jahr. Chem. 1897, **50**, 2800; Arch. des Soc. Biolog. St. Petersb. **7**, 411.

dioxide, acetic and butyric acids, as well as valeric acid in smaller amounts, and a trace of some unidentified higher alcohols.

Although so many workers have obtained crude cultures which were capable of acting on cellulose to give definite decomposition products,[1] yet W. Omelianski was the first to isolate the bacteria and to study the decomposition quantitatively.[2] He demonstrated that pure Swedish filter paper is attacked by certain anaerobic bacteria obtained from river mud, manure or sewage deposits. The fermentation process is very slow compared with ordinary alcoholic fermentations, and it is best carried out at 35° C. in presence of calcium carbonate. The incubation period, before gas is evolved, varies from one week to several months. During fermentation, fatty acids are formed and these gradually dissolve part of the calcium carbonate present. The cellulose is gradually changed into soluble constituents, and at the end of thirteen months a residue was obtained which was only 3.6% of the weight of the cellulose originally present.

There are at least two different types of bacteria capable of converting cellulose into these simple degradation products. In both cases carbon dioxide is formed, but one type of bacteria gives hydrogen while the other gives methane. Normally, the methane fermentation occurs, but if the vitality of the methane-

---

[1] E. Durin, Compt. rend. 1876, **83**, 128, 355; abst. Jour. Chem. Soc. 1877, **31**, 106; Chem. News, 1876, **34**, 63; Mon. Sci. 1876, **18**, 862; Ber. 1876, **9**, 1430, 1446; Chem. Tech. Rep. 1876, **15**, II, 129; Jahr. Chem. 1876, **29**, 947; Zts. Chem. Grossgewerbe, 1876, **1**, 135; J. de Pharm. 1876, **24**, 290, 356. See also L. Pasteur, Compt. rend. 1876, **83**, 176; Chem. Centr. 1876, **47**, 663; Chem. Tech. Rep. 1876, **15**, II, 129; Mon. Sci. 1876, **18**, 862.

[2] V. Omelianski, Compt. rend. 1895, **121**, 653; abst. Jour. Chem. Soc. 1896, **70**, ii, 202; J. S. C. I. 1896, **15**, 129; Biederm. Centr. **25**, 501; Chem. Centr. 1895, **66**, II, 1166; Jahr. Chem. 1896, **49**, 2013. For the action of *Mucor boulard* on starch and cellulose, see Soc. Franc. des Distilleries d l'Indo Chine, F. P. 459634, 459815, 1912; abst. J. S. C. I. 1913, **32**, 1167; C. A. 1914, **8**, 3215. Arch. biolog. St. Petersb. **7**, 411; abst. Chem. Centr. 1900, **71**, I, 918; Jour. Chem. Soc. 1900, **78**, ii, 493; J. S. C. I. 1900, **19**, 679; Jahr. Chem. 1900, **53**, 842; Meyer Jahr. Chem. 1900, **10**, 246; Centr. f. Physiol. 1900, **14**, 33. Centr. Bakt. Parasitenk. 1906, **15**, ii, 673; abst. Chem. Centr. 1906, **77**, I, 1034; J. C. S. 1906, **90**, ii, 188; Rep. Chim. 1906, **6**, 187; Meyer Jahr. Chem. 1906, **16**, 270; Biochem. Centr. 1906–1907, **5**, 494. Centr. Bakt. Parasitenk. 1904, **11**, 369; abst. Jour. Chem. Soc. 1904, **86**, ii, 278; Rep. Chim. 1904, **4**, 379; Chem. Centr. 1904, **75**, II, 825; Jahr. Chem. 1904, **57**, 2126; Zts. ang. Chem. 1904, **17**, 566, 1556. F. Czapek, Beitr. chem. Physiol. u. Pathol, **1**, 538; **2**, 557; **3**, 47; abst. Chem. Centr. 1902, **73**, I, 532; II, 1068; J. C. S. 1902, **82**, ii, 280; 1903, **84**, ii, 35, 168; Bull. Soc. Chim. 1903, (3), **30**, 440, 526, 1278; Chem. Zts. 1902–1903, **2**, 343; Jahr. Chem. 1902, **55**, 1936.

producing organism is reduced or destroyed by previously warming the inoculant, the hydrogen fermentation occurs. The bacilli which bring about the two different types of fermentation are very similar morphologically.

The following table shows Omelianski's results from two experiments.[1]

	Hydrogen Fermentation		Methane Fermentation	
Cellulose:				
Quantity taken	3.4743 gm.		2.0815 gm.	
Undecomposed residue	0.1272 gm.	(3.6%)	0.0750 gm.	(3.6%)
	3.3471 gm.	(96.4%)	2.0065 gm.	(96.4%)
Fermentation products:				
Volatile organic acids	2.2402 gm.	(64.5%)	1.0223 gm.	(49.1%)
Carbon dioxide	0.9722 gm.	(28.4%)	0.8678 gm.	(48.3%)
Hydrogen or methane	0.0138 gm.		0.1372 gm.	
Total products of fermentation	3.2262 gm.		2.0273 gm.	

S. Trotman[2] has called attention to the communication of S. Penticost,[3] on a pink discoloration sometimes caused in cotton cloth by the formation of pseudo-mauveine. Trotman has investigated a similarly appearing case which was due to an entirely different cause, i. e., mould. The goods upon storing for two weeks, gave a faint pink color, microscopical examination disclosing mould which readily developed on starchy matter, particularly in the presence of organic acids, but could not be grown upon gelatin.

The particular bacteria regarded by P. van Tieghem[4] and

---

1. Chem. Ztg. 1902, **26**, 133; abst. Centr. Bakt. Parasitenk. 1902, **8**, ii, 193, 225, 257, 289, 321, 353, 385; abst. J. C. S. 1902, **82**, ii, 468; Chem. Centr. 1902, **73**, I, 732, 887, 945, 1068; J. Russ. Phys. Chem. Soc. 1902, **34**, II, 7; Chem. News, 1901, **84**, 220; J. S. C. I. 1902, **21**, 418; Bull. Soc. Chim. 1902, (3), **28**, 853; Rep. Chim. 1902, **2**, 311, 450; Chem. Ztg. 1902, **26**, 133; Jahr. Chem. 1902, **55**, 1987; Biochem. Centr. 1902–1903, **1**, 157; Arch. d. Sci. Biol. **9**, No. 3.

2. J. S. C. I. 1909, **28**, 1237; abst. C. A. 1910, **4**, 1241; Chem. Zentr. 1910, **81**, I, 1396. Zts. ang. Chem. 1910, **23**, 757; J. Soc. Dyers Col. 1910, **26**, 32.

3. J. S. C. I. 1909, **28**, 1180; abst. C. A. 1910, **4**, 672; Chem. Zentr. 1910, **81**, I, 778.

4. Bull. soc. botan. 1877, **24**, 128; 1879, **25**; Compt. rend. 1879, **88**, 205; **89**, 5, 1102; abst. Chem. News, 1879, **39**, 103; J. C. S. 1880, **38**, 334; Mon. Sci. 1879, **21**, 296; Ber. 1879, **12**, 2087; Chem. Tech. Rep. 1879, **18**,

others as the specific ferment of cellulose, namely *Bacillus amylobacteria*, is not capable, according to Omelianski, of decomposing cellulose. Pure cultures of the special bacteria employed by the latter worker are obtained by the method of selective cultures.[1] To Swedish filter paper and chalk contained in flasks, is added a solution containing the following media, which acts as food for the bacteria: Potassium and ammonium phosphates, magnesium sulfate, a small quantity of gum-arabic and a trace of river-mud. The flask is then hermetically closed and kept at 30°–35° C. Fermentation sets in after a definite interval. The progress of the fermentation is followed by changes which occur in the appearance of the cellulose material. The filter paper first becomes a yellowish color; a transparency and gelatinous stage is reached later, and finally the greater portion of the paper is changed into a soluble condition. Portions of the chalk are also dissolved by the fatty acids formed, and pass into solution as calcium acetate and calcium butyrate. The bacteria remains attached to the small portion of unattacked paper which remains. From the organisms collected on the filter paper, the bacillus is obtained by heating for five minutes to 90°, and then cooling to 37°. These operations of heating followed by cooling are repeated several times. Further cultivations on potatoes are necessary. There is difficulty in obtaining the cellulose-decomposing bacteria in a pure state, as they cannot be isolated by the usual procedure, since they do not grow on solid media. The method of accumulation is usually employed in the elimination of foreign bacteria. The ferment is 6–7 μ long and 0.2–0.3 μ broad. It forms round spores with a diameter of 1 μ.

W. Oechsner de Coninck,[2] treated filter paper in a similar manner to Omelianski, but uses a simpler food media. He employs potassium phosphate and ammonia nitrate with a small proportion of slime or mud. Fermentation starts in four days and proceeds in a manner similar to that recorded by Omelianski. Among the resulting products he identified propionic acid. A

79; Jahr. Chem. 1879, **32**, 1016; Wag. Jahr. 1879, **25**, 817; Jahr. rein Chem. 1879, **7**, 570; Zts. f. Spiritusind. 1879, 329; Zts. Chem. Grossgewerbe, 1879, **4**, 23, 146, 154.

[1] Compt. rend. 1895, **121**, 653; abst. Jour. Chem. Soc. 1896, **70**, ii, 202; J. S. C. I. 1896, **15**, 129; Bied. Centr. **25**, 501; Chem. Centr. 1895, **66**, II, 1166; Jahr. Chem. 1896, **49**, 2013.

[2] Compt. rend. soc. biol. 1916, **79**, 156; abst. C. A. 1917, **11**, 54.

cellulose decomposing organism has also been described by H. Hutchinson and J. Clayton[1] and others.[2] A. Herzen has found aerobic organisms capable of destroying cotton and linen.[3]

The property possessed by cellulose of resisting the action of most bacteria is utilized in the removal of the natural impurities of cotton cloth. B. Levine[4] found that bacterial treatment

---

1. J. Agric. Sci. 1919, **9**, 143; abst. J. S. C. I. 1919, **38**, 381. For data on the deterioration of paper and cellulose by fungi, refer to P. See, Compt. rend. 1917, **164**, 230; abst. C. A. 1917, **11**, 1041; J. S. C. I. 1917, **36**, 449.

2. H. Pringsheim, Zts. physiol. Chem. 1912, **78**, 266; **80**, 376; abst. J. C. S. 1912, **102**, ii, 587; J. S. C. I. 1912, **31**, 531; C. A. 1912, **6**, 2632; Bull. Soc. Chim. 1913, (4), **14**, 398, 458; Chem. Zentr. 1912, **83**, II, 538; Meyer Jahr. Chem. 1912, **22**, 178, 269. See also van Iterson, Centr. f. Bak. u. Parasitenk. **11**, 689; abst. Chem. Centr. 1904, **75**, I, 1338. He exposed cellulose to the action of bacteria for varying lengths of time, and when the decomposition became too vigorous, an antiseptic was added. This checks the development of gas but allows the action of the endoenzymes to continue. After a short period of action of these it is possible to show the presence of cellobiose and dextrose in the degradation products.

3. Compt. rend. soc. biolog. **41**, 140; abst. Ber. 1891, **24**, 163; Jahr. Chem. 1891, **44**, 2331. See Duclaux, *Ibid.* **41**, 163. C. v. Iterson, Centr. Bakt. 1904, **11**, 689; Kon. Akadem. Amsterdam. 1903, 807; Chem. Centr. 1904, **75**, I, 1338. H. Pringsheim and M. v. Markatz (Zts. physiol. Chem. 1919, **105**, 173; abst. J. S. C. I. 1919, **38**, 594-A) have found that diastase is without action on a dextrin prepared from cellulose. Extracts prepared from the stomach, intestines and pancreas of oxen were also unable to decompose the dextrin, from which it is concluded that the hydrolysis of cellulose in the digestive system of these animals is caused by bacteria. For the "Decomposition of Cellulose by the Anaerobic Organism, Spirochaeta cytophaga," see H. Hutchinson and J. Clayton, J. Agric. Sci. 1919, **9**, 143.

4. J. Ind. Eng. Chem. 1916, **8**, 298; abst. C. A. 1916, **10**, 1273; J. S. C. I. 1916, **35**, 687; Chem. Zentr. 1918, **89**, I, 492; Sci. 1915, **41**, 543. J. Hebden, J. Ind. Eng. Chem. 1914, **6**, 714; abst. J. S. C. I. 1914, **33**, 959; C. A. 1914, **8**, 3632. According to Hebden, the yellowing of bleached cotton cloth on steaming or during storage is due to imperfect removal of alcohol-soluble and nitrogenous impurities. B. Levine confirms Hebden with regard to the importance of the nitrogenous impurities, but finds that the ether-soluble impurities have an equally injurious action, whereas the yellowing is not connected in any way with the presence of the alcohol-soluble constituents. Laboratory experiments with different species of bacteria (*Bac. amylolyticus*, *Bac. fimi*, *Bac. bibulus*, *Bac. carotovorus* and *Bac. subtilis*, Ehrenberg) in a nutrient solution containing 1 gm. each of dipotassium phosphate and magnesium sulfate and 2 gm. each of sodium chloride, ammonium sulfate, and calcium hydroxide per liter, showed that the nitrogenous substances and ether-soluble impurities of cotton can be efficiently removed by bacterial action. The bacteria mentioned converted starch sizing only to dextrins and had little action on the alcohol-soluble impurities. Samples of cotton cloth purified by bacterial action and then bleached, showed no yellow coloration when subjected to steam at a pressure of 10 lbs. per sq. in. for 45 mins. Preliminary trials on a large scale for the purification of paper-making stock, cotton yarn, and cotton cloth by bacterial treatment, previous to bleaching, have given promising results, the material being incubated with the bacteria culture for periods ranging from 72 down to 24 hours. See also C. Cross, E. Bevan and J. Briggs, J. S. C. I. 1908, **27**, 260.

might be employed to remove impurities from untreated cotton. A. Deiss has described[1] a means of obtaining a special anaerobic ferment derived from African esparto, which is capable of destroying certain impurities in such raw cellulose material as crude hemp, corn bast, rice, cotton, jute, etc. The fiber is also disintegrated and in a suitable condition for further purification in order to obtain pure cellulose.

The development of mildew[2] or colored spots[3] on cotton goods requires the presence of starchy and nitrogenous material as food for the fungi.[4] The growth is not due to a direct attack on the cellulose complex. Moulds, however, will grow on pure nitrocellulose suspended in water, provided the requisite mineral matter is present and the material placed in the dark.[5]

The possibility of the decomposition of cellulose in the diges-

[1] E. P. 23625, 1909; abst. C. A. 1911, **5**, 2429. A. Deiss and Fournier, F. P. 403518, 1909; abst. C. A. 1911, **5**, 1514; J. S. C. I. 1910, **29**, 84; Mon. Sci. 1910, **73**, 168, 447; 406722, 1909; abst. C. A. 1911, **5**, 1662; Mon. Sci. 1910, **73**, 174; D. R. P. 235852; abst. C. A. 1912, **6**, 1365; Chem. Zentr. 1911, **82**, II, 328; Wag. Jahr. 1911, **57**, II, 500; Zts. ang. Chem. 1911, **24**, 1498. For the fermentation of cellulose giving methane, see Bull. Union des Physicians, 1918, 71. P. van Tieghem, Bull. soc. botan. 1877, **24**, 128; 1879, 25; Compt. rend. 1879, **88**, 205; 1879, **89**, 5, 1102; abst. Chem. News, 1879, **39**, 103; J. C. S. 1880, **38**, 334; Mon. Sci. 1879, **21**, 296; Ber. 1879, **12**, 2087; Chem. Tech. Rep. 1879, **18**, 79; Jahr. Chem. 1879, **32**, 1016; Wag. Jahr. 1879, **25**, 817; Jahr. rein Chem. 1879, **7**, 570; Zts. Spiritusind. 1879, 329; Zts. Chem. Grossgewerbe, 1879, **4**, 146, 154. V. Omelianski,, Compt. rend. 1897, **125**, 970, 1131; Arch. des Soc. Biolog. St. Petersb. **7**, 411; J. C. S. 1898, **74**, i, 291; J. S. C. I. 1896, **15**, 129; 1898, **17**, 60, 171; 1900, **19**, 679; Bull. Soc. Chim. 1898, **19**, 203, 204; Chem. Centr. 1898, **69**, I, 269; 1900, **71**, I, 918; Chem. Ztg. 1897, **21**, 1057; Jahr. Chem. 1897, **50**, 2800. N. Kessener, D. R. P. 290126, 1914; abst. Chem. Zentr. 1916, **87**, I, 350; Chem. Ztg. Rep. 1916, **40**, 102; Zts. ang. Chem. 1916, **29**, 127; J. S. C. I. 1916, **35**, 486.

[2] For this reason mildew does not appear as often on white and colored cloth, as when in the grey (unbleached) condition, which, being sized is much more prone to this defect. When cotton is thoroughly scoured, therefore, there remains only traces of nitrogenous products, and this scarcity of nitrogenous food makes it difficult for the organisms to thrive. An imperfectly scoured cotton may contain as much as 0.5% of nitrogen, equivalent to 3.25% albuminoid bodies, and such cottons are readily attacked by moulds.

[3] S. Trotman, J. Soc. Dyers Col. 1910, **26**, 32; abst. C. A. 1910, **4**, 1393; J. S. C. I. 1909, **28**, 1238; Chem. Zentr. 1910, **81**, I, 1396; Zts. ang. Chem. 1910, **23**, 757.

[4] E. Knecht (J. Soc. Dyers Col. 1905, **21**, 189; abst. J. S. C. I. 1905, **24**, 841; Biochem. Centr. 1905–1906, **4**, 416; Chem. Ztg. Rep. 1905, **29**, 235; Meyer Jahr. Chem. 1905, **15**, 510; Lehne's Faerberztg. 1905, **16**, 313; Leipziger Faerberztg. 1905, **54**, 375; Zts. ang. Chem. 1906, **19**, 303, 1475) has shown that human saliva has a peculiar and distinct action upon cotton cellulose, and that when a piece of bleached calico has previously been saturated with saliva, it will absorb considerably more substantive dyestuffs than untreated cotton. On account of the fact that the saliva loses this power after boiling, the effect has been ascribed to the ptyalin present.

[5] T. Bokorney (Chem. Ztg. 1896, **20**, 985; abst. J. C. S. 1898, **64**,

tive organs of some animals has often been suggested. It is assumed that the cellulose is converted into soluble substances which are assimilated by the animal organism.[1,2,3,4,5,6] According to

---

ii, 39; Chem. Centr. 1897, **68**, I, 30; Jahr. Chem. 1896, **49**, 1031) showed that the bacterial growth is rapid, and a considerable quantity of the vegetable growth accumulates round the masses of cellulose nitrate. He claims that cellulose itself cannot act as a food supply, and it seems probable that if glycerol is present cellulose nitrate is no longer made use of.

1. Cellulose-dissolving Enzyme in Snail Liver, W. Biedermann and P. Moritz, Pflueger's Archiv. 1898, **73**, 219; abst. J. C. S. 1899, **76**, ii, 166; Chem. Centr. 1898, **69**, II, 1214.

2. H. Lohrisch, Digestion of Crude Fiber and Cellulose by Man and Animals, Zentr. ges. Physiol. Path. Stoffwechsels, **21**, 801; abst. C. A. 1908, **2**, 562. Absorption and Nutritive Value of Cellulose and Hemicellulose in Man, Zts. exper. Path. **5**, 478; abst. C. A. 1909, **3**, 1434. Digestion of Cellulose by Dogs, Zts. physiol. Chem. **69**, 143; abst. J. C. S. 1910, **98**, ii, 1083; C. A. 1911, **5**, 936; Chem. Zentr. 1910, **81**, II, 1829.

3. Cellulose Digestion, W. Ellenberger, *et al.*, Zts. physiol. Chem. 1915, **96**, 236; abst. C. A. 1916, **10**, 916; J. C. S. 1916, **110**, i, 588. W. Grimmer and A. Scheunert, Berl. Tierärztl. Wochenschr. 1910, **26**, reprint; Zentr. Biochem. Biophys. **10**, 71; abst. C. A. 1910, **4**, 2531; J. C. S. 1910, **98**, ii, 554; Chem. Zentr. 1910, **81**, I, 1625. Digestion of Cellulose in, and Ferments of, the Caecum, A. Scheunert, Zts. physiol. Chem. 1906, **48**, 9; abst. J. C. S. 1906, **90**, ii, 463; Chem. Centr. 1906, **77**, II, 62. Solubility of Cellulose in Saliva of Sheep, A. Scheunert, Berl. Tierärztl. Wochenschr. 1910, **26**, reprint; abst. C. A. 1910, **4**, 2531; J. C. S. 1910, **98**, ii, 521. "Cellulose Digestion and the Estimation of Cellulose by the Methods of Lange and Simon and Lohrisch," A. Scheunert and E. Lötsch, Zts. physiol. Chem. 1910, **65**, 219; abst. C. A. 1910, **4**, 2312; J. C. S. 1910, **98**, ii, 464; J. S. C. I. 1910, **29**, 555; Chem. Zentr. 1910, **81**, I, 1851; Jahr. Chem. 1910, **63**, II, 421; Zts. ang. Chem. 1910, **23**, 1389. Cellulose Digested by Dog? A. Scheunert and E. Lötsch, Biochem. Zts. 1909, **20**, 10; abst. C. A. 1910, **4**, 64, 2531; J. C. S. 1909, **96**, ii, 905; Chem. Zentr. 1909, **80**, II, 1265. Digestion of Cellulose in Domestic Animals, A. Scheunert, H. Lötsch and W. Grimmer, Berl. Tierärztl. Wochenschr. 1909, **26**, 5, 113; abst. C. A. 1910, **4**, 2169, 2530; J. C. S. 1910, **98**, ii, 520; Chem. Zentr. 1910, **81**, I, 1625; Jahr. Chem. 1910, **63**, II, 420.

According to S. Acree (Pulp and Paper Mag. 1919, **17**, 569; abst. J. S. C. I. 1919, **38**, 677-A), very serious losses may be caused by the rotting of wood in stacks. Calculated on the basis of equal volumes of sound and rotten woods, a loss of 75% of wood substance has been recorded after 12 months. A block of sound spruce wood contains 58% of its weight of cellulose; in a similar block of rotten wood only 13%–14% of cellulose was found, equivalent to a loss of 76% of the original cellulose. The methoxyl group, from which wood alcohol is formed, has been destroyed to the extent of 75%; the acetic acid group, 80%; the pentosan, 77%, and the methylpentosan, 65%. These constituents had been converted into gases and soluble substances; the matter soluble in hot water had increased by 146%. The fungi and bacteria infect the stacks in certain parts. Some of them get through into the (mechanical) pulp and growths of red or black patches appear in the pulp is inferior in color and strength to that made from sound pulp. Estimates made at pulp mills indicate losses of wood amounting to 5%–10% through rotting, and in addition, losses of strength in the pulp of 10%–20%, or in some cases even 50%. The fungus of "red rust" has been isolated and studied in the form of cultures.

4. H. Weiske and T. Mehlis, Digestion of Cellulose by Geese, Landw. Versuchst. **21**, 411; abst. Jour. Chem. Soc. 1878, **34**, 905; Chem. Centr. 1878,

I. Dreyfus,[1] however, certain organisms such as *Polyporus, Agaricus campestris, Bacillus subtilis,* pus bacilli and *Aspergillus glaucus,* contain cellulose.

W. Tappeiner[2] analyzed the gases from the intestines of herbivorous animals, and found them to consist of carbon dixoide and methane with smaller quantities of hydrogen. To test if organized ferments brought about the decomposition of cellulose, he placed pure cellulose, in the form of absorbent cotton or pulp of the finest vellum paper, with a food medium (1% meat extract). He sterilized the mixture and then added a small quantity of pancreas extract of bovine origin. A vigorous fermentation set in and carbon dioxide and methane were evolved in some experiments. In others the gases evolved were carbon dioxide and hydrogen. In control-experiments where the pancreas extract was absent no gas was evolved.[3]

E. Knecht[4] and J. Huebner[5] have observed that bleached

49, 504; Jahr. Chem. 1878, **31,** 987.

5. Nutritive Value of Cellulose, N. Zuntz, Pflueger's Archiv. **49,** 477, 483; Bied. Centr. 1892, **21,** 88; abst. J. C. S. 1893, **64,** ii, 22; Ber. 1891, **24,** R, 837; Chem. Centr. 1891, **62,** II, 383; Jahr. Chem. 1891, **44,** 2258; 1892, **45,** 2193; Meyer Jahr. Chem. 1892, **2,** 281. See also A. Mallevre, Pflueger's Archiv. **49,** 460; abst. J. C. S. 1893, **64,** ii, 21; Mon. Sci. 1891, **37,** 76; Ber. 1891, **24,** R, 836; Chem. Centr. 1891, **62,** II, 381; Chem. Ztg. Rep. 1891, **15,** 197; Jahr. Chem. 1891, **44,** 2258. von Henneberg and Pfeiffer, Jour. f. Landwirtschaft, 1890, **38,** Part 2. W. von Tappeiner, Zts. f. Biol. **24,** 118. N. Zuntz and Lehmann, Landw. Jahr. 1889, 41, 153. A. von Werther, Zts. d. Ver. f. Ruebenzuckerind. 1886, 426. Pfeiffer and Lehmann, Jour. f. Landw. 1886, 239. J. Munk and T. Rosenheim, Verhandlungen der physiolog. Ges. Berlin, Feb. 27, 1891.

6. Cellulose Digestion by Enzymes, E. Newcombe, Botan. Centr. 1898, **73,** 105; Annals of Bot. 1899, **13,** 49; abst. J. C. S. 1900, **78,** ii, 99; Chem. Centr. 1899, **70,** II, 129; Chem. Ztg. Rep. 1898, **22,** 72; 1899, **23,** 102; Jahr. Chem. 1899, **52,** 2590; Meyer Jahr. Chem. 1899, **9,** 226.

[1] Zts. physiol. Chem. 1893, **18,** 358; abst. J. C. S. 1894, **66,** ii, 24; Chem. Centr. 1893, **64,** II, 941; Jahr. Chem. 1893, **46,** 879; Chem. Ztg. Rep. 1893, **17,** 271.

[2] Amer. J. Sci. 1883, (3), **26,** 404; Ber. 1882, **15,** 999; abst. Chem. News, 1884, **50,** 260; J. C. S. 1882, **42,** 985; Bull. Soc. Chim. 1882, **38,** 44; Chem. Ztg. 1882, **6,** 494; Jahr. Chem. 1882, **35,** 1202; Bied. Centr. **13,** Part 4.

[3] C. Beadle and H. Stevens, J. S. C. I. 1909, **28,** 1018; abst. C. A. 1910, **4,** 482, 1100; Paper Trade J. (4), **50,** 52; Bull. Soc. Chim. 1910, **8,** 523; Rep. Chim. 1910, **10,** 112; Chem. Zentr. 1910, **81,** I, 779; Jahr. Chem. 1909, **63,** II, 383; Wag. Jahr. 1909, **55,** II, 527; Zts. ang. Chem. 1910, **23,** 852. For the decomposition of cellulose in the presence of bacteria, see E. Meusel, Ber. **8,** 1215, 1356, 1653; Compt. rend. 1875, **81,** 95; abst. Chem. News, 1875, **32,** 204; 1876, **33,** 262; J. C. S. 1876, **29,** 189, 413; Jahr. Chem. 1875, **28,** 172, 898; Jahr. rein chem. 1875, **3,** 20.

[4] J. Soc. Dyers Col. 1905, **21,** 189; abst. J. S. C. I. 1905, **24,** 841; Biochem. Centr. 1905–1906, **4,** 416; Chem. Ztg. Rep. 1905, **29,** 235; Meyer

calico which is saturated with saliva absorbs more coloring matter than untreated calico. If the saliva is previously boiled its effect is lost. Diastase has also an action, but to a less degree.[1] Knecht assumes that an enzyme ptyalin in the saliva is the active principle. The solution of the vegetable cell walls during germination is attributed to a special ferment (cytase),[2] by J. Grüss.

The conversion of the cellulose into soluble compounds is probably brought about by destructive ferments present in the digestive tract. H. Bierry and J. Giaja[3] obtained from the alimentary tract of various invertebrates certain enzymes which were capable of hydrolyzing cellulose and polysaccharides. V. Hofmeister[4] introduced freshly mown grass enclosed in a suitable apparatus into the rumen of a sheep. In three days he found that 78.4% of the 21.6% of fiber present in the grass had been removed. Experiments were carried out comparing the solvent action of gastric juices and liquid manures on grass-fiber. The gastric juices dissolved 78.8%, while an equal amount of the liquid manure dissolved only 3.5% of the fiber. The amount of hay dissolved by gastric juice, is proportionate to the amount of the latter solvents present. The solvent action of gastric juice mixed with glycerol and saliva from various glands on cellulose, was also investigated. The greatest amount of fiber dissolved (80.4%)

Jahr. Chem. 1905, **15**, 510; Lehne's Faerberztg. 1905, **16**, 313; Leipziger Faerberztg. 1905, **54**, 375; Zts. ang. Chem. 1906, **19**, 303, 1475.

5. J. Huebner, J. S. C. I. 1908, **27**, 105; Proc. Manch. Lit. Phil. Soc. 1908, **52**, 2; abst. C. A. 1908, **2**, 1187, 1347; Chem. News, 1908, **97**, 10; Proc. Chem. Soc. 1907, **23**, 304; Bull. Soc. Chim. 1908, **4**, 1060; Rep. Chim. 1908, **8**, 238; Chem. Zentr. 1908, **79**, I, 1097; Chem. Ztg. 1908, **32**, 220; Jahr. Chem. 1905–1908, II, 3185; Meyer Jahr. Chem. 1908, **18**, 505; Wag. Jahr. 1908, **54**, II, 467; Zts. ang. Chem. 1908, **21**, 87, 1760.

[1] Scheurer, Bull. Soc. Ind. Mulhouse, 1903, **73**, 320; abst. J. S. C. I. 1904, **23**, 57; Mon Sci. 1903, **59**, 704; Chem. Ztg. 1903, **27**, 772.

[2] Wochenschrift f. Brauerei, 1895, **12**, 1257; J. Landw. **43**, 379; abst. J. C. S. 1896, **70**, ii, 669; J. S. C. I. 1896, **15**, 464; Chem. Centr. 1895, **66**, I, 787; 1896, **67**, I, 313; Chem. Ztg. Rep. 1895, **19**, 71; 1896, **20**, 48; Jahr. Chem. 1895, **48**, 2681; 2701; J. Landw. 1896, **43**, 379. Wochenschrift f. Brauerei, 1902, **19**, 243; abst. J. C. S. 1902, **82**, i, 713; J. S. C. I. 1902, **21**, 715; Chem. Centr. 1902, **73**, I, 1277; Jahr. Chem. 1902, **55**, 1989; Wag. Jahr. 1902, **48**, II, 410.

[3] Biochem. Zts. 1912, **40**, 370; abst. C. A. 1912, **6**, 2116; J. C. S. 1912, **102**, ii, 657; J. S. C. I. 1912, **31**, 561; Bull. Soc. Chim. 1913, **14**, 331; Chem. Centr. 1912, **83**, II, 199.

[4] Arch. Wiss. Prakt. Thierheilk, 1881, **7**, 169; abst. Bied. Centr. 1881, 669; abst. J. C. S. 1882, **42**, 237.

occurred in the experiment where mixed saliva was employed.

Experiments with sheep by F. Lehmann[1] with a Pettenkofer respiration apparatus, indicated that cellulose as a food was equal to starch material, as far as increase in the production of lean meat was concerned; cellulose, however, was much inferior as a fat producer. O. Kellner, et al.,[2] carried out a very detailed experimental study of the assimilation of cellulose by herbivorous animals. He concluded that straw cellulose, from which the lignone constituents had been removed, has a nutritive value equal to that of starch as far as flesh formation was concerned.

In the breaking down of cellulose in the digestive tract, it is probable that compounds other than methane, hydrogen, carbon dioxide and fatty acid were formed. These intermediate decomposition products have probably a large nutritive value. They are assimilated in this stage by the animal organism.[3]

Analytical Examination of Cellulose Raw Materials.[4] 1. *Gen-*

---

1. Lehmann, Exper. Stat. Record, 1895, **7**, 235; Land. Jahr. 1895, **24**, 117; J. C. S. 1896, **70**, ii, 262.

2. Landw. Versuchs-Stat. 1900, **53**, 1474; abst. J. C. S. 1900, **78**, ii, 566; Chem. Centr. 1900, **71**, I, 992, 994.

3. G. Lusk, Amer. J. Physiol. 1911, **27**, 467; abst. J. C. S. 1911, **100**, ii, 311; Chem. Zentr. 1911, **82**, I, 1227. A. deBary, Ann. Sci. Nat. Botan. 1863, (4), **20**, 1. Bot. Ztg. 1886, **44**, 377, 393, 409, 433, 449, 465. J. Behrens, Centr. Bak. Para. u Infektion. 1898, **4**, II, 514, 547, 577, 635, 700, 739. M. Berthelot, Compt. rend. 1889, **109**, 841. Bertrand, Gabriel and M. Holderer, Ann. l'Inst. Pasteur, 1910, **24**, 180. E. Bourquelot, Bull. soc. Mycol. 1893, **9**, 230. J. Choukevitch, Ann. l'Inst. Pasteur, 1911, **25**, 247 P. Deherain, Ann. Agronom. 1884, **10**, 385. A. Distaso, Compt. rend. soc. Biol. 1911, **70**, 995. U. Gayon, Compt. rend. 1884, **98**, 528. Mem. soc. Sci. Phys. et Nat. Bord. 1884, (3), **1**, LI, LVII. Ber. Verter König. Sach. 1859, 104. A. Hebert, Ann. Agronom. 1892, **18**, 536. J. Henneberg, Zts. Biol. 1885, **21**, 613. K. Kellerman and I. McBeth, Centr. Bak. Para. u Infektion. 1912, **34**, II, 485. W. von Knieriem, Zts. Biol. 1885, **21**, 67. Lehmann, Franz and J. Vogel, J. Landw. 1889, **37**, 251. Macfayden, Allan and F. Blaxall, Trans. Jenner Inst. Prev. Med. 1899, (2), 162, R, 186. W. Nylander, Bull. Soc. Bot. 1865, **12**, 395. W. Omelianski, Centr. Bak. Para. u Infektion. 1902, **8**, II, 193, 225, 257, 289, 321, 353, 385; 1904, **11**, II, 369, **12**, II, 33; 1906, **15**, II, 673. L. Popoff, Pflüger's Archiv. 1875, **10**, 113. J. Reiset, Compt. rend. 1856, **42**, 53. H. Schellenberg, Flora, 1908, **98**, 257. T. Schloesing, Compt. rend. 1889, **109**, 835. Ann. Agronom. 1892, **18**, 5. A. van Senus, Jahr. Gähr. Organ. 1890, **1**, 136. E. Smith, Sci. 1902, **15**, 405. A. Trecul, Compt. rend. 1865, **61**, 156; 432; 1867, **65**, 521. L. Tulasne, Ann. Sci. Nat. Bot. 1854, (4), **2**, 77. H. Ward, Ann. Bot. 1888, **2**, 319; 1898, **12**, 565. H. Weiske, Zts. Biol. 1870, **6**, 456; 1888, **24**, 553. Chem. Centr. 1884, **55**, 385. K. Weiske, B. Schulze, and Flechsig, Zts. Biol. 1886, **22**, 373.

4. This topic in its entirety has been contributed by J. F. Briggs, Research Chemist, British Cellulose & Chemical Manufacturing Co.

It will be remembered that this author's contributions cover the entire domain of cellulose and cellulose derivatives as indicated by the following:

eral Discussion: The chemical constitution of all plant structures capable of serving as raw materials for the cellulose industries varies within sufficiently narrow limits to admit of one general scheme of analytical investigation. Nevertheless, within these narrow qualitative limits there remains room for wide variations in quantitative relationships among certain well defined types. Close conformity to chemical type is a strong characteristic of all species in the vegetable world. The constitutional units of the plant structure may be grouped under three main complexes: the Cellulose complex, the Lignin complex and the Cutin complex. Depending on these complexes as colloids in the natural state, there are factors such as moisture, mineral matters, etc., which move with them, but in addition to these there is a whole range of transitory components and localized deposits, such as sugars, tannins, resins, coloring matters, proteins, etc., which from the present point of view may be dismissed as non-constitutional or adventitious and, though frequently important and valuable in themselves, they have no significance in the valuation of cellulose raw materials. Such components are often conveniently classed together under the general denomination of "extractives," and sometimes it is convenient to express analytical results calculated on the material free from moisture, ash, fat and extractives.

The components of the main constitutional complexes may

J. Briggs, "Cellulose as a Polysaccharide," J. S. C. I. 1909, **28,** 340. "Absorption of Sodium Hydroxide by Cellulose Hydrate," Chem. Ztg. 1910, **34,** 455. "Hydration of Cellulose in the Beating Process and Nature of Cellulose Hydrates," Papierfabrikant, 1910, **8,** Fest u. Auslandsheft, p. 46. "Tendering of Linen in Presence of Copper," J. S. C. I. 1911, **30,** 397. "Microscopic Details of Certain Wood Pulps," World's Paper Trade Review, 1911; abst. J. S. C. I. 1911, **30,** 1374. "Action of Oxalic Acid on Cellulose," J. S. C. I. 1912, **31,** 521. "Acid Tendering of Nitro Artificial Silks," Faeber. Ztg. 1913, **24,** 75. "Cellulose Esters of Benzoic Acid," Zts. ang. Chem. 1913, **26,** 255. "System of Paper Testing," Papierfabrikant, 1914, **12,** Fest u. Auslandsheft, 25. "Bleaching of Linen and Cotton Textiles," J. S. C. I. 1916, **35,** 78. "The paper Mill Chemist in War Time," J. S. C. I. 1916, **35,** 798. "Progress in the Analysis of Cellulose and Cellulose Derivatives," Analyst, 1915, **40,** 107. (With R. Balston) "Manufacture of Soluble Acetylized Cellulose Derivatives," E. P. 10243, 1903. (With C. Cross and E. Bevan) "Cellulose Acetosulfates," Ber. 1905, **38,** 1859, 3531. "Xanthogenic Esters of Starch," Chem. Soc. Trans. 1907, **91,** 612. "Color Reactions of Lignocelluloses," Ber. 1907, **40,** 3119. "Phloroglucinol Absorption of Lignocellulose. Estimation of Ground Wood Pulp," Chem. Ztg. 1907, **31,** 725. "Chloramine Reactions of Proteins (Flax Bleaching)," J. S. C. I. 1908, **27,** 260. "Fibrous Cellulose Acetates," J. Soc. Dyers Col. 1908, **24,** 189.

be regarded as existing in many stages of molecular aggregation, condensation or polymerization, manifested as components of inferior and superior resistance to hydrolytic agencies. A classification in this sense has been suggested by J. König and E. Rump,[1] who proposed the prefixes "proto" for the components of least resistance removable by boiling with water under pressure, "hemi" for those of intermediate resistance removable by boiling with dilute mineral acids under pressure, and "ortho" for those of superior resistance. This is a very convenient nomenclature applicable both to the cellulose and lignin complexes, but the divisions are purely arbitrary and only capable of definition in terms of the conditions of time, concentration and temperature which govern the actual percentages of material removed by hydrolysis.

The Cellulose Complex. In the widest sense of the word, the cellulose complex may be defined as comprizing all the polysaccharide carbohydrates which form an essential portion of the structure of the plant and which yield cupric reducing sugars on hydrolysis with acids. From this definition starch would be excluded, functioning as stored-up sugar and belonging rather to the circulatory system than to the plant structure. The polysaccharides fall into two main groups: the Pentosans, yielding pentose sugars on hydrolysis, and the Hexosans, yielding hexose sugars; normal cellulose itself being the most resistant of the hexosans. The definition of "Cellulose" in a narrower sense is a question around which much controversy has been waged. The cellulose complex comprizes superior and inferior members of the hexosan and pentosan groups, some of which become detached in the processes of isolation and purification. With this circumstance in view, cellulose may be defined as the resistant residue from a series of carefully regulated process of attrition by methods of selective extraction, oxidation and hydrolysis, sufficient to effect the complete removal, in the mildest possible manner, of the other constitutional complexes, together with all adventitious and extractive matters. Those members which succumb to the most careful treatment belong to the group of hemicelluloses, while the resistant residue is the purified cellulose, itself a com-

---

[1] Zts. Nahr. u. Genussmittel, 1914, **28**, 188; abst. J. S. C. I. 1915, **34**, 1203; C. A. 1915, **9**, 815.

plex product which may comprize both hexosan and pentosan members and divisible into α-cellulose (more resistant) and β-cellulose (less resistant). The degree of resistance of any of the members, however, is in no case absolute, but only relative. Degradation of substantial portions of the β-cellulose and of smaller portions of the α-cellulose takes places more or less in the manufacture of cellulose by industrial processes, according to the severity of the treatment required for purification, and indeed, can hardly be avoided even in analytical processes in the laboratory. This conception of cellulose as itself a complex residue from purification introduces the necessity of admitting variations in nature and composition according to the species of plant from which the cellulose was derived. These variations due to species follow well defined classifications, and we have to deal with natural types represented, for example, by cotton cellulose, flax cellulose, the cellulose of grasses (straw and esparto) and the cellulose of woods, which last are again naturally subdivided into woods of coniferous and deciduous or broad-leafed types.

Further, any analytical definition of cellulose must conform to some ideal of technical utility, the first object of such being the establishment of an analytical basis for the control of the processes of production, by affording a comparison between the total amount of cellulose present in the material and that realizable on the industrial scale under the limitations imposed by commercial conditions. The practical problem in this sense is to determine for any given plant material the maximum yield of purified cellulose possessing all the physical and chemical qualities recognized as characteristic of the species of the optimum. The second object of technical utility is the characterization of natural variations of chemical type, in order that the cellulose may be properly placed in the chemical groups to which it belongs and its commercial value from a chemical point of view estimated. In any method for estimating cellulose it is necessary to eliminate those inferior members of the cellulose complex which, from a technical point of view, are not entitled to rank either with the α-cellulose or the β-cellulose. The method of this exclusion can only be empirically established as a controlled process of hydrolysis, because the hemicelluloses are only differentiated from their celluloses by their inferior resistance to hydrolysis. In the absence of any generally agreed specification some authorities have considered it advizable to omit any intentional hydrolytic treatment for the elimination of hemicelluloses, relying only on what occurs unavoidably in the process of removing the lignin. In such cases the yield of cellulose would be high, but the presence of inferior constituents in the cellulose would have to be reckoned with. Other authorities, on the other hand, notably J. König,[1] have gone so far in the elimination of hemicelluloses as virtually to destroy the quality of the cellulose. In such cases the yield of cellulose is low and may even be lower than the commercial yield, thereby defeating the technical utility which is the object of the analytical estimation.

For an account of the nature and relative proportions of the various hemicelluloses in the two main classes of woods, reference may be made to a publication by J. König and E. Becker,[2] who have described the analysis of the mixtures of sugars produced by the hydrolysis of the hemicelluloses by dilute mineral acids. The hemihexosans yield dextrose, mannose and small quantities of galactose and the hemipentosans yield exclusively xylose. These analyses also show that the coniferous woods contain substantial quantities of mannan, while the hemicelluloses of broad-leafed woods consist principally of xylan.

In the present scheme of analytical discussion the constituent described by the older authorities under the name of "wood gum," extracted from plant materials by digestion with 5% sodium hydroxide in the cold is intentionally passed over, first because the extraction of hemicelluloses by this treatment is not complete and has no quantitative significance, and secondly because the extract undoubtedly comprizes a portion of the lignin. On similar grounds of indefinite constitution the application of the term "pectose" or "pectin" to the structural components of cellulose raw materials is also avoided, the substances originally

[1] Zts. Nahr. u. Genussmittel, 1903, **6**, 774; abst. J. C. S. 1903, **84**, ii, 764; Rep. Chim. 1904, **4**, 19; Chem. Centr. 1903, **74**, II, 1147; Chem. Ztg. 1903, **27**, 614; Chem. Zts. 1903–1904, **3**, 481; Jahr. Chem. 1903, **56**, 1015. Zts. Nahr. u. Genussmittel, 1906, **12**, 385; abst. J. C. S. 1906, **90**, ii, 905; J. S. C. I. 1906, **25**, 1069; Rep. Chim. 1907, **7**, 46, 93; Chem. Centr. 1906, **77**, II, 1529; Chem. Ztg. 1906, **30**, 1159; Chem. Zts. 1907, **6**, 143; Jahr. Chem. 1905–1908, II, 968; Zts. ang. Chem. 1907, **20**, 543.

[2] Zts. ang. Chem. 1919, **32**, 155.

designated under that name being more appropriately characterized as hemicelluloses.

The Lignin Complex. The chemical constitution of this most characteristic component of woody substance still awaits a convincing elucidation. The only investigators who have attempted to give approximate and speculative accounts of its constitutional structure are C. Cross and E. Bevan[1] on the one hand, and P. Klason[2] on the other. Both authorities are agreed as to the presence of an aromatic or hydroaromatic nucleus to which many of the particularly striking color reactions of lignin are to be referred. This portion of the complex shows relationships and analogies to the tannins, with catechol as an ultimate derivative; lignin, in fact, has been described as a kind of insoluble tannin. Lignin reacts as an unsaturated compound; it is readily oxidizable, combines with halogens to form characteristic products, with nitrous acid to form bright yellow nitroso compounds, and with sulfurous acid or bisulfites to form sulfonic acids. With caustic soda, on heating, soluble sodium salts of definitely acid derivatives are formed. All these reactions are actually utilized to convert lignin into a soluble form and liberate the cellulose, but only that depending on the combination with halogens is of general analytical significance, both for qualitative and quantitative purposes. By this reaction a perfectly clean and complete separation of the lignin from the cellulose complex is attained with the minimum of hydrolytic attack on the latter.

Lignin is not a carbohydrate and contains no alcoholic hydroxyl groups capable of esterification. It is condensed rather than hydrolyzed by strong mineral acids which break down the cellulose complex completely into soluble products, and this resistance forms the basis of an analytical method for the estimation of lignin as an insoluble residue.

The *Methoxyl group* is a characteristic function of the lignin complex, capable of exact determination in the form of methyl iodide by Zeisel's method. The quantity of lignin, however, can-

---

[1] J. Soc. Dyers Col. 1916, **32**, 135; abst. J. S. C. I. 1916, **35**, 628; C. A. 1916, **10**, 2303.

[2] "Beiträge zur Kenntniss der chemischen Zusammensetzung des Fichtenholzes," Berlin, 1911. Ark. Kemi. Min. o. Geol. 1917, **6**, 21; abst. J. S. C. I. 1919, **38**, 570-A. Svensk. Kem. Tidskrift. 1917, **29**, 5, 47; abst. C. A. 1917, **11**, 2482. Cf. C. Schwalbe and E. Becker, Zts. ang. Chem. 1919, **32**, 155, 229.

not be calculated from the methoxyl value because this differs in different types of lignin. M. Hönig and J. Spitzer,[1] for instance, have detected in the same wood, lignins differing greatly in the percentage of methoxyl group combined. T. von Fellenberg[2] considers that the methoxyl group is characteristic of "pectin" as well as of lignin, and has proposed a method for the separate estimation of the two types of methoxyl, that from pectin being liberated by dilute acids and that from lignin only by strong acids. Although this distinction has been endorsed by C. G. Schwalbe,[3] who applies it for the estimation of "pectin" in woods and other plant structures, its justification and utility have not been demonstrated, and the vague definition of "pectin," as applied to these materials, probably covers only the more readily soluble hemihexosans and hemipentosans, together with the lignin combined with them.

The *Acetic Acid group*, which is regarded as the source of the pyroligneous acid formed by the destructive distillation of wood, is a characteristic component of woody, i. e., lignified, plant tissues generally, and may consequently be classed as an adjunct of the lignin complex rather than of the cellulose. It is, however, liberated by the mildest hydrolytic treatments, even by digestion with steam, and has never been definitely localized as attached to either of the major complexes when these are separated. The actual quantity of acetic acid obtainable on hydrolysis is variable according to the chemical pre-treatment of the raw material,[4] and it may be assumed that under certain circumstances part of the acetic acid must be derived from other groups not only of the lignin, but also of the cellulose. In this sense the precise constitutional significance of the acetic acid group remains ill-defined; nevertheless, by adopting standard conditions of hydrolysis, the yield of acetic acid may be established as an analytical constant of specific importance.[5]

The Cutin Complex. The cutin complex composes the ex-

---

[1] Monatsh. 1918, **39**, 1; abst. J. S. C. I. 1918, **37**, 502-A.

[2] Mitt. Lebensmittelunters. u. Hyg. 1916, **7**, 42; abst. J. C. S. 1916, **110**, ii, 351; C. A. 1916, **10**, 2772.

[3] Zts. ang. Chem. 1919, **32**, I, 125.

[4] C. Cross and E. Bevan, J. Soc. Dyers Col. 1916, **32**, 135; abst. J. S. C. I. 1916, **35**, 628.

[5] A. Schorger, J. Ind. Eng. Chem. 1917, **9**, 556, 561; abst. C. A. 1917, **11**, 2218; J. S. C. I. 1917, **36**, 867; Ann. Rep. Soc. Chem. Ind. 1917, **2**, 144.

ternal cuticular covering of all plants. This region ranges in dimensions from bulky masses, represented by cork, to membranes of infinite thinness. All cuticular tissues, fulfilling the natural function of water repulsion, namely that of keeping sufficient moisture in and excess of water out, show an exudation of free fat, fatty acid or wax, which is determined by simple extraction with solvents. When this free fat is removed, there remains the parent complex, the cutin proper, which appears to be composed of cellulose esters of fatty and resin acids.[1] This complex is closely associated with the complexes of the lignocellulose, but the nature of the association, whether constitutional or merely mechanical, is not known. The cutin ester resists most of the ordinary chemical treatments, but it is saponified and broken down into its components by alcoholic sodium hydroxide. A method for the estimation of cutin has been recommended by J. König,[2] based on its insolubility in cuprammonium reagent or in acid zinc chloride solution, but the satisfactory application of this method is somewhat difficult, since it involves the previous removal of the lignin without attacking the cutin. C. G. Schwalbe[3] has stated that if the structural complexes of the plant material be first broken down by heating with hydrochloric acid so as to obtain a friable powder, the quantity of free fat, wax or resin extractable by volatile solvents is very considerably increased, in some cases doubled.

2. *Qualitative and Preliminary Examination.* Tests for Lignification.—One of the first steps in the examination of a raw material is to obtain an idea of the extent of lignification and to ascertain whether the lignified structure is general or local. The most useful test for this purpose is the phloroglucinol-hydrochloric acid reagent, which gives an intense crimson stain with *raw* lignin,

---

[1] C. Cross and E. Bevan, J. Soc. Dyers Col. 1919, **35**, 70; abst. J. S. C. I. 1919, **38**, 249-A.

[2] Zts. Nahr. u. Genussmittel, 1906, **12**, 385; abst. J. C. S. 1906, **90**, ii, 905; J. S. C. I. 1906, **25**, 1069; Rep. Chim. 1907, **7**, 46, 93; Chem. Centr. 1906, **77**, II, 1529; Chem. Ztg. 1906, **30**, 1159; Chem. Zts. 1907, **6**, 143; Jahr. Chem. 1905–1908, II, 968; Zts. ang. Chem. 1907, **20**, 543.

[3] Zts. ang. Chem. 1919, **32**, I, 125. In this connection refer also to A. Besson, Chem. Ztg. 1917, **41**, 346. Lindner, Zts. ang. Chem. 1919, **32**, 56. C. Schwalbe, Papierfabr. 1908, **6**, 551. Zts. ang. Chem. 1918, **31**, 193. C. Schwalbe and W. Schulz, "Ueber die Aufschlieszung pflanzlicher Rohstoffe mittels Salzsäure," 1917, p. 25; Chem. Ztg. 1918, **42**, 229; abst. Zts. ang. Chem. 1918, **31**, 125. G. Testone, Staz. sperim. agarar. ital. **50**, 97; abst. Chem. Zentr. 1918, **89**, II, 865. D. R. P. 309555, 1917.

but is by no means to be relied upon with materials which have been chemically treated. The reagent is most economically prepared by dissolving 0.5 gm. of phloroglucinol in 50 cc. of water and then adding 50 cc. of strong commercial hydrochloric acid. The material to be examined is steeped in a little alcohol and then covered with an equal volume of the phloroglucinol reagent. The maximum color is developed in a few minutes, but appears more slowly if no alcohol be used. It is not advizable to mix alcohol with the original reagent, as sometimes recommended, since its keeping properties are thereby impaired. Lignin gives characteristic colors with a large number of aromatic amines and phenols, the bright yellow stain developed on treatment with solutions of aniline salts being largely employed. A test much in favor with certain workers is Maule's reaction, according to which the material is steeped for a few minutes in potassium permanganate, washed, decolorized with 12% hydrochloric acid, again washed and treated with a little ammonia solution. Lignin then shows a deep red coloration. The most characteristic and delicate test for lignin, whether raw or as a residue after chemical treatments, is the chlorine-sodium sulfite reaction.

Alkaline Hydrolysis. The method originally introduced by C. Cross and E. Bevan[1] for the preliminary classification of fibrous raw materials still affords useful general indications. The material is boiled with 1% solution of sodium hydroxide (α) for five minutes, (β) for one hour, the volume of the liquid being kept constant. The results are quantitatively expressed as loss of weight of the fibrous residue calculated on the dry substance. The indications of this test cannot be defined in terms of any particular constituents of the material. The loss in the short period of 5 minutes may be held to comprize mainly extractive matters in general, sugars, starch, resin, tannins, etc., and this figure serves to afford a zero point from which to measure the indications of the longer treatment. The difference between the two may be taken as a measure of the readily hydrolyzable components of the major constitutional complexes and comprizes the inferior hemicelluloses, together with the lignin associated with them. It must be remembered, however, that the separations

---

[1] "Miscellaneous Vegetable Fibers," C. Cross, Reports of Colonial and Indian Exhibition, 1886.

are not sharp or specific, and that what is measured is in fact a certain region on the curve indicating the rate of hydrolysis of the entire material.

Chlorination and Isolation of Ultimate Fibers. The elegant reaction discovered and applied by C. Cross and E. Bevan for the quantitative estimation of cellulose may be utilized in its qualitative application for the isolation of the ultimate fibers, vessels and cells which compose the masses or strands of raw plant tissues. In the majority of cases the cohesion of these constituent elements can only be broken down by the removal of the lignin, and Cross and Bevan's chlorination reaction effects this in the most complete and simplest manner. The manipulation follows closely the lines indicated for the quantitative estimation of cellulose (*q. v.*) but the preliminary disintegration of the material need not be so complete for the present purpose. Nevertheless, in the case of massive materials such as wood, it is necessary to afford free exposure to the chlorine gas by shredding, rasping, shaving, or otherwise opening up the tissues before the chemical treatment. After chlorination, the chlorolignin compound is decomposed and extracted by boiling with 2% sodium sulfite solution, the action of which for qualitative purposes may be considerably accelerated by the addition of a little caustic soda to the boiling solution. With a little mechanical assistance, the material falls apart into its constituent elements composed of substantially pure cellulose and the felted mass is collected on a cotton filter, washed, pressed, and preferably kept in the moist state for microscopical examination.

Examination of Cellulose Fibers. Certainly in those industries which utilize cellulose in virtue of its structural properties, the microscopic characteristics are fundamental, and are not to be neglected in those industries which only regard cellulose as a chemical raw material. The microscopical identification of cellulose fibers for the diagnosis of species is a specialized branch of study which is outside the present subject, but in any case it is important to ascertain the structural homogeneity or heterogeneity of the pure cellulose prepared from the material. Thus it is necessary to establish the presence or absence of fibers of abnormal development, the density and thickness of the cell walls and the relative proportions of fibrous and non-fibrous elements. All these are contributory factors which may considerably influence the uniformity of the chemical reactions in industrial applications with pure cellulose as a basis. The chemical reactivity of a mass of cellulose which is not structurally homogeneous is governed by the reaction velocity of its most resistant members and in so far as this is dependent on processes of diffusion and other physical factors, a knowledge of the microscopic structure is of great importance.

The cellulose carefully prepared by the chlorination process should be completely free from lignin, but in many cases the cutin complex is but little attacked by the operations described. If now the preparation be treated with cuprammonium solution (Schweizer's reagent), the cellulose is rapidly dissolved, leaving the cuticular elements in the form of an insoluble residue. The microscopic examination of this residue may afford confirmatory evidence of identification and, if the quantity is substantial it will have to be taken into account from an industrial point of view.

3. Quantitative Methods. **Moisture.** The exact determination of hygroscopic moisture in cellulose materials has been investigated and discussed by M. Renker.[1] The problem is simplest in the case of pure or approximately pure cellulose, but becomes increasingly complicated in the case of materials containing high proportions of unsaturated oxidizable constituents, such as lignin or resins, or of volatile essential oils. Renker proposes as the basic standard of hygroscopic moisture the loss in weight sustained on exposure in a vacuum desiccator over phosphorus pentoxide at a temperature not exceeding 35° C. until constant weight is attained. Equilibrium, however, is reached only slowly, and an exposure of at least 20 hours is required.

For practical purposes, among which may be included all industrial applications, as well as the formulation of a dry weight basis for the calculation of the results of other analytical factors, the ordinary method of drying in a steam-heated oven at 98°–105° C. to constant weight has been generally accepted and formally approved.[2] The time of heating required ranges from 4 to 6 hours. It is important that the dried sample be placed in

[1] "Ueber Bestimmungsmethoden der Cellulose," Berlin, 1909.

[2] Ver. der Zellstoff und Papier Chemiker, Hauptversammlung, 1909, 133.

a weighing bottle with close-fitting stopper *before* removing from the oven and be allowed to cool in the desiccator before weighing, as dried cellulose is extremely hygroscopic.

It has been remarked that the errors and the difficulty of arriving at a constant dry weight increase the further the composition of the material is removed from that of pure cellulose. In dealing with materials rich in resin and volatile oils the method of distillation with a hydrocarbon may be adopted and has the additional advantage that a large sample is used for the determination. This method is advocated by C. G. Schwalbe.[1] Fifty to one hundred gm. of the shredded material are placed in a tin-lined copper distillation flask and covered with about 200 cc. of petroleum of suitable boiling point. The liquid is boiled and after one-fourth or one-third of the hydrocarbon has distilled, the whole of the moisture will have passed over into the receiver. This is so constructed that the volume of the aqueous layer can be accurately read off after the separation is complete by allowing the water to settle out from the petroleum distillate in the graduated lower portion of the receiver. A. Besson[2] has described an improved form of distillation vessel and receiver for the estimation of moisture in this manner.

Oil, Fat, Wax and Resin. For the estimation of these constituents the only method is by extraction with volatile organic solvents in a Soxhlet or equivalent continuous extraction apparatus, an operation requiring at least six hours.

The amount of fatty or resinous matter varies with the nature of the solvent employed. Ether is the solvent most generally and conveniently used, but it is also the one which gives the lowest yield of extractive matter. C. G. Schwalbe[3] recommends exhaustive extraction with ether, followed by extraction with absolute alcohol. The alcoholic extract may, however, contain other matters besides the true fat, wax and resin groups, and

---

1. Zts. ang. Chem. 1908, **21**, 400, 2311; abst. C. A. 1908, **2**, 1885, 2448; 1909, **3**, 406; J. C. S. 1908, **94**, ii, 627; J. S. C. I. 1908, **27**, 294; Bull. Soc. Chim. 1908, **4**, 633; 1909, **6**, 58; Chem. Zentr. 1908, **79**, I, 1336; II, 447; Jahr. Chem. 1905–1908, II, 960; Meyer Jahr. Chem. 1908, **18**, 504; Wag. Jahr. 1908, **54**, II, 492. Zts. ang. Chem. 1919, **32**, 125. "Die Chemie der Cellulose," 1911, 612.

2. Chem. Ztg. 1917, **41**, 346; abst. J. S. C. I. 1917, **36**, 671. Schweiz. Apoth. Ztg. 1917, **55**, 69; abst. C. A. 1917, **11**, 1613.

3. Zts. ang. Chem. 1919, **32**, 125.

may include substances soluble in water. An alternative method, also favored by Schwalbe and less tedious than the double extraction, consists in extracting the material with a mixture of equal volumes of alcohol and benzene. This mixture is to be preferred because the influence of the benzene may be expected to prevent the extraction by the alcohol of the water-soluble substances referred to above.

Whatever solvent be employed, the material should be thoroughyl dried in the air before extraction; drying in the oven is to be avoided as the heating tends to render some of the resins insoluble.[1] Schwalbe has indicated that the results of extraction with volatile solvents are largely subject to the factor of penetration and has shown that if the structure of the material be completely broken down by a preliminary treatment with hydrochloric acid, a very much larger quantity of fat or resin is extracted by volatile solvents than in the case of the raw material. This process, however, requires further standardization.

Aqueous Extract. Various plant materials contain various percentages of constituents soluble in cold or hot water. While this factor is easily demonstrable, it is distinctly difficult in quantitative application. The groups soluble in cold water comprize sugars, tannins, coloring matters, etc., while those soluble in hot water include starch, pectin and some of the nitrogenous matters. The principal difficulty encountered in the quantitative estimation of these groups is the mechanical difficulty of effective penetration, even when the material is thoroughly prepared by crushing or rasping. To facilitate penetration, the operation should be carried out on material which has been freed from fat and resin by extraction with volatile solvents, but even then the resistance of the cutin layer to water persists almost unimpaired.

A further complication occurs with regard to extraction with hot water owing to the fact that the process does not halt at simple extraction, but extends to the hydrolysis of the more sensitive constituents of the major complexes. Thus, while overcoming the difficulty of defective penetration the loss of substance by conversion into soluble products of hydrolysis is continuous with the duration of boiling. The time of boiling with water

---

[1] C. Schwalbe and W. Schulz, Chem. Ztg. 1918, **42**, 229; abst. C. A. 1918, **12**, 2253, 2450; J. S. C. I. 1918, **37**, 382-A.

must therefore be limited and specified and should not exceed a period of three hours. The loss of weight is determined after drying the residual material in the oven and is calculated on the dry raw material.[1]

Alkaline Hydrolysis. The processes of α-hydrolysis and β-hydrolysis, carried out as described on page 356 in a quantitative manner, afford important information on the general quality of a raw material, but the treatment is not sufficiently specific for a quantitative measure of any characteristic group of constituents. It is possible, however, to effect a complete isolation of the cellulose by digestion with caustic soda solution under pressure in an autoclave, and this method is often adopted in the laboratory, not so much for an analytical determination of the total cellulose present, as for studying the best conditions of treatment in industrial working. The yield of cellulose thus obtained represents the practical yield under the conditions adopted and is always considerably less than the theoretical yield obtained by analytical methods. The amount of this difference depends on the severity of the treatment necessary to liberate the cellulose from the lignin, during which the β-cellulose components are progressively hydrolyzed.

The concentration of the caustic soda solution employed for this digestion ranges from 2% to 4% of NaOH and the temperature from 130° to 170° C., corresponding to pressures of 25 to 95 lbs. per sq. in. This test digestion is generally accompanied by periodical determinations of the quantity of sodium hydroxide neutralized by the acidic products of the hydrolysis, mainly lignic and acetic acids, together with lactonic acids derived from the carbohydrates when high temperatures have been employed. The procedure usually adopted is to draw off portions of the alkaline liquor at stated intervals during the digestion and to estimate by titration the total soda after evaporation and incineration of one part of the sample, using methyl orange, and the "free" soda directly in another part of the sample, using phenolphthalein as indicator. The decrease in the ratio of "free" to total soda is a measure of the progress of the reaction, and when the difference between consecutive samples becomes small and constant the end

---

[1] A. Schorger, J. Ind. Eng. Chem. 1917, **9**, 556, 561; abst. C. A. 1917, **11**, 2218; J. S. C. I. 1917, **36**, 867; Ann. Rep. Soc. Chem. Ind. 1917, **2**, 144.

of the digestion is indicated, except in special instances.

Cellulose. The classical chlorination reaction of Cross and Bevan has been almost unanimously adopted as the basis of all the analytical methods for the quantitative estimation of cellulose in raw and partly purified materials, but, although the agreement in principle is general, the actual manipulation has been variously modified by individual workers. The treatment consists in exposure of the moist material to an atmosphere of chlorine gas and the subsequent decomposition and extraction of the chlorinated lignin by boiling sodium sulfite solution.

The difficulties of the process are all traceable to mechanical obstacles, that is, the resistance of the denser colloidal tissues to the penetration of the gas. For this reason the removal of the lignin is only rarely completed in one operation, and it is necessary to repeat the alternate chlorination and extractions with sulfite until the residual cellulose no longer shows a perceptible coloration during the treatment. Thus any deficiency in mechanical disintegration has to be made good by chemical attrition, and it may easily happen that serious chemical losses of cellulose may occur by excessive exposure to the attack of the chlorine.

It is understood, therefore, that before making the analyses the sample must be suitably prepared by mechanical means according to its nature, in order to present the minimum resistance to the penetration of the gas, for instance, by crushing and opening out any hard portions or, in the case of woods, by taking thin shavings or fine raspings.

The chemical manipulations may be described according to two different schemes although, as mentioned above, several variations are possible.

(a) *Cross and Bevan's method.* This original scheme differs from most of those which have subsequently been proposed in that the raw material is previously submitted to a chemical preparation before exposure to the chlorine gas. This pre-treatment consists in boiling the raw material for one hour with a 1% solution of sodium hydroxide; that is to say, it undergoes the β-alkaline hydrolysis. One effect of this is to eliminate the gummy colloidal carbohydrates included under the general term of "hemicelluloses," comprizing hemihexosans and hemipentosans, and to exclude them *ab initio* from the cellulose definition. A certain amount of misapprehension has arisen on this point owing to the fact that the yield of "cellulose" is lowered by the alkaline pre-treatment and higher values are obtained by its omission,[1] but it may be contended that carbohydrates which cannot survive the simple process of β-hydrolysis are not entitled to rank as cellulose and are more correctly eliminated at the start than at a later stage. Incidentally the alkaline treatment removes the portion of the lignin which is associated with the hemi-celluloses and considerably facilitates the chlorination of the remainder by opening up the harder tissues to the access of the gas. Thus the chemical pre-treatment supplements the mechanical preparation and reduces the number of chlorinations required to arrive at a pure product.

Cross and Bevan's manipulation is adapted for dealing with relatively large samples of the raw material, for instance, not less than 5 gm. nor more than 10 gm. of the air-dry substance. The sample is first covered with a 1% solution of sodium hydroxide and the liquid is boiled for exactly one hour (Cross and Bevan specify half an hour) under a reflux condenser. The residue is collected on a cotton cloth filter, washed with hot water and pressed. It is then teased out and treated in a closed bottle with a current of washed chlorine gas. The bottle should be immersed in a freezing bath and the duration of the first chlorination should not exceed one hour. The object of these precautions is to restrict the hydrolyzing action of the hydrochloric acid which is formed in large quantities in the first chlorination treatment; in fact, if more than a single chlorination is required in any case, it is better to limit the duration of the first to half an hour. After chlorination, the material is quickly treated with a solution of sulfurous acid or a sulfite and washed to neutrality on the cotton filter. The substance is then transferred to a 2% solution of sodium sulfite in which the characteristic crimson coloration is developed, and the liquid is boiled for about half an hour. The fiber, now largely liberated, is again collected on the filter, washed, pressed and subjected to a second chlorination of shorter duration, followed by a second extraction of the chlorinated lignin with hot sulfite solution.

With loose fibers, such as jute, hemp, etc., a single treatment

---

[1] M. Renker, "Bestimmungsmethoden."

is sufficient to remove all the lignin and with denser materials the number of chlorinations required depends on the perfection of the preliminary preparation. The purified cellulose is finally bleached with highly dilute sodium hypochlorite or permanganate, soured, washed and weighed after drying in the oven.

(b) *Sieber and Walter's Method.* It is to be noted that the chemical pre-treatment with boiling alkali according to the method described above, is only recommended in the case of raw plant materials in order to remove hemi-celluloses and so-called "pectins." In the case of partially purified materials, such as commercial wood celluloses, which have already undergone fairly severe hydrolytic treatments, the alkaline hydrolysis is not legitimate. The tendency in recent times has been (wrongly, in our opinion) to omit the alkaline pre-treatment even in the case of raw materials, including that of raw wood. This omission affords a slightly increased yield of cellulose as it leaves in a portion of the hemicellulose. The method described by R. Sieber and L. Walter[1] in its application to wood is representative of this other scheme of procedure and has received endorsement by various workers.[2]

By this method all the operations are performed in a porcelain Gooch crucible having a perforated porcelain plate fitting loosely inside the bottom. This plate is stitched between two pieces of fine cotton fabric and the cotton is trimmed off round the edge to fit tightly in the bottom of the crucible. The raw wood material is very finely powdered by means of a rasp and sifted so that the portion which passes through a 75-mesh sieve but not through a 100-mesh is taken for the analysis. This fine mechanical subdivision considerably facilitates the chemical reactions but necessitates the employment of relatively small quantities for the analysis. Not more than 1 gm. of the air-dry powder is weighed out into the previously dried and tared Gooch crucible, which is then suspended in hot alcohol in order to extract the resin. The alcohol is washed out with hot water on the suction pump and the contents of the crucible are partially dried

---

[1] Papierfabr. 1913, **11**, 1179; abst. J. S. C. I. 1913, **32**, 974; C. A. 1914, **8**, 1202; Zts. ang. Chem. 1914, **27**, II, 311. Cf. A. Dean and G. Tower, J. A. C. S. 1907, **29**, 1119.

[2] B. Johnsen and R. Hovey, J. S. C. I. 1918, **37**, 132-T; Paper, 1918, **21**, 136; abst. C. A. 1918, **12**, 1250, 1598; Ann. Rep. Soc. Chem. Ind. 1918, **3**, 134. See also C. Schwalbe and E. Becker, Zts. ang. Chem. 1919, **32**, I, 230.

by passing a current of dry air through the mass. Afterwards the crucible is connected with a supply of washed chlorine gas, which is passed through the cake of moist wood meal for the required time. When the treatment is finished the material is treated with sulfurous acid, washed and the crucible is suspended in a bath of hot sodium sulfite solution (3%) in which it is digested for one hour. All these operations are performed consecutively without removing the material from the Gooch crucible; all the filtrations are assisted by the suction pump, but care must be taken not to suck the wood powder down to a hard cake against the filter plate. The alternate chlorination and digestion treatments are repeated until the lignin reaction is no longer indicated. With suitably powdered wood the purification of the cellulose may be effected with four chlorinations, lasting respectively for 20, 15, 15 and 10 minutes.

The cellulose prepared by the chlorination process from the majority of raw plant materials is not a homogeneous substance and is not to be regarded as chemically equivalent to purified cotton cellulose. It is a complex of α- and β-celluloses containing both hexosan and pentosan constituents.

Furfural Value or Pentosans. The polysaccharides of pentosan constitution are important members of the cellulose complex and, like the hexosans, may be represented as groups presenting various degrees of resistance to hydrolytic attack, and although a portion of these constituents is eliminated with the hemi-celluloses, a residue of the more resistant types remains not only in the cellulose prepared by chlorination, but also to some extent in that purified by industrial processes.

The quantitative measurement of pentosan groups is based on the condensation reaction induced by aqueous hydrochloric acid on the pentose molecule whereby furfural is produced. The reaction has been developed into an analytical method of considerable accuracy by B. Tollens and his colleagues, and a complete description of the conditions to be observed is given by W. Kroeber.[1] These conditions must be accurately followed, as the

---

[1] J. Landw. 1901, **48**, 357; **49**, 7; abst. J. C. S. 1901, **80**, i, 371; ii, 288; J. S. C. I. 1901, **20**, 396; Chem. Centr. 1901, **72**, I, 477, 1119; Jahr. Chem. 1901, **54**, 885, 886; Zts. anal. Chem. 1908, **47**, 520. See also W. Kroeber, C. Rimbach and B. Tollens, Zts. ang. Chem. 1902, **15**, 477, 508; abst. J. C. S. 1902, **82**, ii, 537; J. S. C. I. 1902, **21**, 875; Rep. Chim. 1902, **2**, 475; Chem. Centr. 1902, **73**, II, 76; Jahr. Chem. 1902, **55**, 1049, 1050.

method in its quantitative application is substantially empirical.

A suitable quantity of the air-dry material, chosen so that the weight of furfural phloroglucide to be obtained shall not exceed 0.3 gm., is placed in a distillation flask of about 350 cc. capacity fitted with a dropping funnel and connected with a condenser. The material is covered with 100 cc. of 12% hydrochloric acid (sp. gr. 1.06) and the liquid is heated slowly at first and then distilled at such a rate that 30 cc. of the acid distils in 10–15 minutes. The drops of distillate are allowed to fall into the receiver through a small filter to remove traces of volatile fats. After 30 cc. of distillate has been collected, the same quantity of fresh acid is introduced through the dropping funnel and the distillation is continued at the same rate with repeated additions of acid so that the volume of liquid in the flask remains substantially constant. Alternatively the dropping funnel may be so adjusted that fresh acid is continually dropping into the flask as fast as the distillate is driven off. Care must be taken to wash down with fresh acid any particles of the material thrown on to the side of the flask and protection should be provided to prevent the overheating of the walls of the flask; a shallow bath of fusible metal may be used for heating. When 360 cc. of distillate has been collected, the whole of the furfural should have come over and a drop of the distillate should no longer show a red spot when tested with aniline-sodium acetate reagent. The entire distillate is then treated with a solution of pure phloro glucinol, free from diresorcinol, in 12% hydrochloric acid, the quantity of phloroglucinol used being double the weight of the expected furfural. The mixture is stirred, made up to 400 cc. with 12% hydrochloric acid and set aside to stand over night. The amorphous greenish black precipitate is collected in a tared Gooch crucible fitted with an asbestos pad and washed with 150 cc. of cold water in such a way that the cake is not completely drained until the washing is completed. It is then dried for four hours in the oven at 100° C. and weighed in a well closed weighing bottle, as the dried phloroglucide is extremely hygroscopic. The weight of the phloroglucide is then expressed in terms either of furfural or pentosans by the application of factors given by Krœber as follows:

(a) For weight of phloroglucide "w" between 0.03 and

0.300 gm., the following formula is to be used:

Furfural = $(w + 0.0052) \times 0.5185$
Pentosan = $(w + 0.0052) \times 0.8866$

(b) For weight of phloroglucide "w" less than 0.03 gm.

Furfural = $(w + 0.0052) \times 0.5170$
Pentosan = $(w + 0.0052) \times 0.8949$

(c) For weight of phloroglucide "w" above 0.300 gm.

Furfural = $(w + 0.0052) \times 0.5180$
Pentosan = $(w + 0.0052(\times 0.8824$

A more rapid method for the precipitation of the furfural phloroglucide has been described by K. Boddener and B. Tollens,[1] whereby the precipitate is formed in hot solution instead of cold. Three hundred cc. of the acid distillate are treated with phloroglucinol (double the calculated quantity +0.15 gm.) also dissolved in 12% hydrochloric acid. The volume is then made up to 400 cc. with 12% hydrochloric acid and the liquid is heated to 80°-85° C., then allowed to stand at the ordinary temperature for $1^1/_2$-2 hours. It is then filtered off in the Gooch crucible, washed with 150 cc. of water, dried for 4 hours in the water oven, placed in a weighing bottle, cooled in the desiccator and weighed. The phloroglucide thus obtained has a different composition from that precipitated in the cold and the factor for calculating to furfural is 0.571.

Methylpentosan. A minor portion of the phloroglucide precipitate consists of the methylfurfural derivative which may be separated by extracting the weighed precipitate of total phloroglucides with warm 95% alcohol according to the method of W. Ellett and B. Tollens.[2] The extraction is made in an apparatus resembling a Soxhlet apparatus in which the Gooch crucible containing the precipitate is suspended, as described by M. Ishida and B. Tollens.[3] The passage of the alcohol is continued until the extract flows through practically colorless, which takes only a short time. The residue, consisting of furfural phloroglucide, is dried and weighed back, the difference in weight being reck-

---

1. J. Landw. 1910, **58**, 232; abst. C. A. 1911, **5**, 736; J. S. C. I. 1911, **30**, 242; Chem. Zentr. 1911, **82**, I, 127.
2. Zts. Ver. Zuckerind. 1905, **55**, 19; Ber. 1905, **38**, 492; abst. J. C. S. 1905, **88**, ii, 210; J. S. C. I. 1905, **24**, 212; Bull. Soc. Chim. 1906, **36**, 619; Chem. Centr. 1905, **76**, I, 834; Chem. Ztg. Rep. 1905, **29**, 48, 75; Jahr. Chem. 1905–1908, II, 957; Zts. anal. Chem. 1909, **48**, 166; Zts. ang. Chem. 1905, **18**, 1541.
3. J. Landw. 1911, **59**, 261; abst. C. A. 1911, **5**, 2508; J. C. S. 1911, **100**, ii, 645; J. S. C. I. 1911, **30**, 1181; Chem. Zentr. 1911, **82**, II, 794.

oned as methylfurfural phloroglucide. The corrected value for furfural phloroglucide is calculated according to Krœber's formula (above) and the methylfurfural phloroglucide is calculated to methylpentose by a formula given by W. Mayer and B. Tollens[1] for fucose where "w" is the weight of phloroglucide in milligrams.

$$\text{Mgrms. Methylpentose} = 2.6595\,W - 0.01226\,W^2 + 0.586$$
$$\text{Methylpentosan} = \text{Methylpentose} \times 0.89.$$

Acetic Acid Group. It has been noted that the quantity of acetic acid obtainable from lignified materials is subject to variation according to the method of treatment employed. Consequently, when applying this factor as a characteristic of species, it is desirable that the conditions of hydrolysis should be as simple as possible and strictly defined. E. Schorger[2] has described the following procedure, which has been adopted for the examination of woods: 2 gm. of the powdered raw material are boiled under a reflux condenser with 100 cc. of 2.5% sulfuric acid for 3 hours. The volume of the liquid is then made up to 250 cc. and an aliquot portion of the filtered hydrolyzed solution is distilled under vacuum. The volatile acid in the distillate is titrated with standard sodium hydroxide and calculated in terms of acetic acid; it will, however, include a minor proportion of formic acid.

Methoxyl Group. This factor is estimated by the classical method of Zeisel, as described by R. Benedict and M. Bamberger,[3] and modified by G. Gregor,[4] whereby the material is completely broken down by boiling with concentrated hydriodic acid and the methoxyl converted into methyliodide, which is absorbed in alcoholic silver nitrate solution and decomposed into

---

[1] Ber. 1907, **40**, 2434, 2441; abst. C. A. 1907, **1**, 2562, 3062; 1908, **2**, 674; J. C. S. 1907, **92**, ii, 586; J. S. C. I. 1907, **26**, 781; Bull. Soc. Chim. 1908, **4**, 435, 464; Rep. Chim. 1907, **7**, 399, 426; Chem. Zentr. 1907, **78**, II, 301, 302, 745; Jahr. Chem. 1905–1908, II, 858; Meyer Jahr. Chem. 1907, **17**, 135; Zts. anal. Chem. 1908, **47**, 322; Zts. ang. Chem. 1908, **21**, 28.

[2] J. Ind. Eng. Chem. 1917, **9**, 556, 561; abst. C. A. 1917, **11**, 2218; J. S. C. I. 1917, **36**, 867; Ann. Rep. Soc. Chem. Ind. 1917, **2**, 144.

[3] Monatsh. 1890, **11**, 260; abst. Chem. News, 1892, **65**, 21; J. C. S. 1890, **58**, 1474; J. S. C. I. 1890, **9**, 1156; Bull. Soc. Chim. 1891, **5**, 535; Ber. 1890, **23**, R, 649; Chem. Centr. 1890, **61**, II, 608; Chem. Ztg. 1890, **14**, 872; Jahr. Chem. 1890, **43**, 255; Wag. Jahr. 1890, **36**, 1156; Zts. ang. Chem. 1890, **3**, 741; Zts. anal. Chem. 1891, **30**, 636.

[4] Monatsh. 1898, **19**, 116; Wien. Akad. Ber. **107**, 140; abst. J. C. S. 1898, **74**, ii, 490; J. S. C. I. 1898, **17**, 609; Bull. Soc. Chem. 1899, **22**, 191; Chem. Centr. 1898, **69**, II, 510, 831; Chem. Ztg. Rep. 1898, **22**, 149; Jahr. Chem. 1898, **51**, 841; Oest. Chem. Ztg. 1898, **1**, 253, 288.

silver iodide, and after drying, the material is carefully weighed.

The apparatus comprizes a special distillation flask of about 50 cc. capacity, having a long neck capable of serving as a reflux air-cooled condenser. Two side tubes are fused into the neck, about 20 cm. apart, the lower one serving for the introduction of a slow current of CO_2 gas and the upper one for the discharge of the methyl iodide vapors. A CO_2 generator (marble and hydrochloric acid), delivering gas through washing vessels containing silver nitrate solution in the first and strong sulfuric acid in the second, is attached to the lower branch of the distillation flask, while the upper branch is attached to a U-shaped gas-washing bulb tube containing a few cc. of a 10% solution of potassium carbonate and arsenious acid. The U-tube is suspended in a beaker of water heated at 50°–60° C. This solution absorbs vapors of hydriodic acid and iodine which may be carried over, while the CO_2 containing the methyl iodide vapors passes through into two absorption flasks, the first of which contains 50 cc. and the second 25 cc. of an alcoholic solution of silver nitrate, previously standardized with $N/10$-thiocyanate, and containing a few drops of nitric acid. The silver solution is prepared by dissolving 17 gm. of silver nitrate in 30 cc. of water and diluting to one liter with absolute alcohol.

A quantity of the material which will yield about 0.1–0.2 gm. of silver iodide is placed in the distillation flask with 20 cc. of hydriodic acid of sp. gr. 1.70, which represents the aqueous solution of the acid of constant boiling point of 127° C. The current of CO_2 is adjusted at a slow-rate and the acid is caused to boil gently. The zone of condensation in the long neck of the flask should be maintained at about one-third of its total length and no hydriodic acid should distil over. Ebullition and passage of CO_2 gas should be continued for at least 3 hours or until no further precipitate is obtained on inserting a test-tube containing alcoholic silver solution in the place of the absorption flasks. When the operation is completed the clear liquid in the first absorption flask is decanted off into a 250 cc. gauged flask, the precipitate is washed several times with cold water and the washings are added to the bulk of the liquid in the 250 cc. flask. The contents of the second absorption flask are also added and the whole is made up to 250 cc. and filtered through a dry paper into a dry receiver. For the titration of the excess of silver nitrate, 100 cc. of the filtrate are treated with nitric acid and ferric sulfate, then titrated in the usual way with $N/10$ thiocyanate.

An alternative procedure in which the titration in the presence of alcoholic liquids is avoided is as follows: The absorption flasks are charged with alcoholic silver nitrate without the addition of nitric acid. The methyl iodide then forms a double compound of silver nitrate and iodide. After the distillation is complete the contents of the absorption flasks are mixed together and the alcohol is distilled off. Nitric acid is then added, the double salt is decomposed by boiling and the excess of silver nitrate is titrated with thiocyanate without filtering off the silver iodide, which does not interfere with the accuracy of the titration.

The silver iodide found is usually calculated in terms of the methyl group (CH_3) expressed on the dry weight of raw material, but it must be understood that only groups containing methoxyl are determined by this method. A novel method of estimating the methyl iodide by means of pyridine, forming the methiodide of a quaternary base has been described by J. Hewitt and W. J. Jones.[1]

Lignin. The direct estimation of the lignin as a residue depends on the total hydrolysis and removal of the cellulose complex. This may be effected either by sulfuric acid of 72% concentration or by hydrochloric acid of 42% concentration (1.21 sp. gr.). J. König and E. Becker[2] have investigated comparatively four different methods for the estimation of lignin in this manner. In all cases the previous removal of the resin, etc., by extraction with alcohol-benzene is necessary. The sulfuric acid method does not give such concordant results as the hydrochloric acid methods and the latter are therefore to be preferred. One of these, the method of R. Willstätter and L. Zechmeister[3] requires a solution of hydrochloric acid gas in concentrated hydrochloric acid saturated at 0° C.; the concentration is thereby raised to 42%. A modification of the method of H. Krull in

[1] J. C. S. 1919, **115**, 193; abst. C. A. 1919, **13**, 1438.

[2] Zts. ang. Chem. 1919, **32**, I, 155.

[3] Ber. 1913, **46**, 2401; abst. C. A. 1913, **7**, 3413; J. C. S. 1913, **104**, i, 955; J. S. C. I. 1913, **32**, 822; Bull. Soc. Chim. 1913, **14**, 1354; Chem. Zentr. 1913, **84**, II, 1209.

which hydrochloric acid gas is used is described by König and Becker as follows: One gram of wood powder which has been extracted with alcohol-benzene to remove resins is moistened with 6 cc. of water in a wide, thick-walled test-tube and hydrochloric acid gas is conducted into the mass, while cooling in an ice-bath, until no further change is apparent and the mass is converted into a thin, deeply colored fluid. The liquid is then allowed to stand for at least 24 hours to complete the hydrolysis until cellulose can no longer be detected by microscopic examination, after which it is diluted with water and the lignin residue is collected in a Gooch crucible, washed and dried. The dry weight of lignin is corrected by incineration and weighing the ash.

In all these operations it is an important point of the manipulation to avoid the formation of a thick paste in which particles of the original material are enclosed by gelatinized cellulose and protected from the complete action of the acid.

Chlorine Absorption. P. Waentig and W. Gierisch[1] have proposed to measure the degree of lignification by the quantitative estimation of the amount of chlorine fixed by the lignin when the finely powdered material is treated with an excess of the moist gas. The material is placed in a small U-tube with ground glass stoppers, which is connected on the inlet side with a supply of chlorine gas and a gas-washing vessel charged with 10% hydrochloric acid. Attached to the exit side is a second U-tube charged with calcium chloride which serves to retain the moisture carried over from the reaction tube. The apparatus is weighed before and after the passage of the chlorine gas and the quantity of chlorine fixed, both as lignin chloride and hydrochloric acid, is found by the increase in weight after sweeping out the excess of chlorine. The quantity of lignin in the material is then calculated by assuming a chlorine factor for pure lignin of 144.

Phloroglucinol Absorption. This indirect method for the estimation of lignin groups was devised by C. Cross, E. Bevan and J. Briggs,[2] and depends on the determination of the quantity of pure phloroglucinol absorbed by the lignified material from a solution of definite concentration in the presence of aqueous

---

1. Zts. ang. Chem. 1919, **32**, 173; abst. J. S. C. I. 1919, **38**, 530-A.
2. "Textbook of Papermaking," 4th Edition, London, 1916, p. 397.

hydrochloric acid. The following are the solutions required:

(a) *Standard phloroglucinol solution.* 2–5 gm. of purest crystallized phloroglucinol are dissolved in 250 cc. of water and the solution is made up to 500 cc. with hydrochloric acid of commercial strength.

(b) *Formaldehyde solution.* 1 cc. of commercial 40% "formalin" is added to a mixture of 250 cc. of commercial hydrochloric acid with 250 cc. of water.

(c) *Aqueous hydrochloric acid.* Equal volumes of commercial hydrochloric acid and water.

Two grams of the finely divided raw material are dried in the oven and weighed; the dry weight is corrected for ash and the material is placed dry in a dry flask together with 40 cc. of the standard phloroglucinol solution. The flask is allowed to remain corked, for at least 16 hours at the ordinary temperature. The time factor for the test is regulated according to the resistance to penetration of the material. After the absorption is complete, the phloroglucinol solution is filtered off through a plug of glass wool and 10 cc. are withdrawn for the titration of the excess of phloroglucinol. This liquid is diluted with 20 cc. of the aqueous hydrochloric acid, heated in a water-bath to 70° C. and titrated with formaldehyde solution in small quantities at a time. After each addition of formaldehyde the flask must be returned to the water-bath for two minutes to allow the precipitate to form. Towards the end of the titration smaller quantities of formaldehyde solution are added, namely, 0.1–0.2 cc., but the period of two minutes should be allowed each time. The end point is indicated by spotting a drop of the liquid on a piece of newspaper, on which the phloroglucinol forms a pink stain, and the titration is finished when no trace of pink is shown after rapidly drying the spot. The difference between the titer of the original phloroglucinol solution and that of the filtered product indicates the weight of phloroglucinol absorbed by the material. This is calculated as a percentage of the corrected dry weight which is expressed as the phloroglucinol absorption value and may be referred to a standard wood meal containing 28% of lignin and showing a phloroglucinol value of about 8%.

Examination of Isolated Cellulose. Celluloses isolated by industrial processes may be examined by methods closely similar to those enumerated for the raw materials with only comparatively slight modifications, as enumerated herein.

The estimations of *moisture*, *ash*, *fat* or *resin* are carried out as already described.

Residual Lignin. The examination for residual lignin may be performed in various ways. The malachite green test has been devised by the chemists of the British War Office for the purpose of detecting traces of lignin residues which are localized or irregularly distributed throughout the mass of purified cellulose and depends on the selective attraction or mordanting action of the lignin towards basic dyestuffs. The reagent is prepared by dissolving 0.1 gm. of the pure basic dyestuff in hot water and diluting to 500 cc. then adding to this solution one containing 50 cc. of commercial 40% formalin and 1 gm. of sodium bisulfate and diluting to one liter with water. Three grams of the cellulose are heated with 300 cc. of the malachite green-formaldehyde solution in the boiling water-bath for ten minutes. At the end of that time 25 cc. of a clear solution of bleaching powder at a concentration of 20 gm. per liter are added to the colored liquor. The excess of dyestuff is thereby destroyed and the cellulose is allowed to steep for a further five minutes in the hot liquid. The liquid is then filtered off and the residual cellulose is rinsed, pressed and examined. In this way any specks or fibers of lignified material show up as bright green particles against a white cellulose background, and the quantity may be estimated by inspection or by comparison with a standard material.

The best method of testing for traces of lignin when the distribution is general rather than localized is by applying the chlorination reaction and noting the amount of pink color developed after transferring the chlorinated fiber to a solution of sodium sulfite sufficiently strong to neutralize the acidity developed on the fiber. The comparison may also in this case be made with a standard preparation of cellulose similarly exposed to chlorine gas and developed with sodium sulfite in a separate dish. The acidity produced by chlorination under standard conditions may be titrated and employed as a measure for comparing the sample with a standard cellulose similarly chlorinated.

Pure Cellulose. The pure cellulose contained in a sample of commercial cellulose may also be estimated by the chlorination reaction carried out, with all the precautions previously described for raw materials, on the crude cellulose after the extraction of the fat and resin with volatile solvents. The procedure is the same as that indicated in the case of raw materials with the exception that the preliminary hydrolysis with boiling 1% sodium hydroxide should be omitted when dealing with a cellulose which has been isolated by industrial chemical processes.

Bleaching Test. A. Baker and J. Jennison[1] have recommended the following standard bleaching test for commercial samples of sulfite wood celluloses: Ten grams of air-dry cellulose are suitably disintegrated, for instance, by beating up with water and draining to a known degree of moisture. The requisite quantity of standardized bleaching powder solution, selected so that only a slight excess shall remain unused at the end of the test is diluted in a wide mouth stoppered bottle with water sufficient to bring the total quantity of liquid used for the 10 gm. of cellulose up to 160 cc. The temperature of the liquid in the bottle is then adjusted at exactly 105° F. (41° C.) and the moist cake of cellulose is dropped in. The cellulose is thoroughly disintegrated by shaking the bottle and the whole is digested at 100° F. (38° C.) for two hours. At the end of that time the pulp is poured on a Buchner filter so as to form a cake of uniform thickness; it is there washed, drained, pressed and subsequently dried. The filtrate and washings are made up to a uniform bulk of 2 liters and the excess of bleach liquor contained therein is ascertained by titration. In this way the consumption of bleaching powder, the color of the bleached sheet and the loss of weight are recorded.

α-Cellulose and β-Cellulose. The separation of α-cellulose and β-cellulose in a commercial pulp or crude cellulose isolated from lignified raw materials can only be made on arbitrary rather than on scientific lines. The inferior members of the cellulose complex present in such preparations may comprize not only those constituents of the original β-cellulose which have survived the processes of isolation and purification but also newly formed compounds of inferior type which have been produced by the degradation, by hydrolysis or oxidation, of the α-cellulose as the

---

[1] J. S. C. I. 1914, **33**, 288; abst. C. A. 1914, **8**, 2944; Zts. ang. Chem. 1915, **28**, II, 224.

result of the unavoidable destructive action of the chemicals employed and, in quantity, depending on the severity of these processes.

The method worked out in the laboratory of Cross and Bevan for the separation of the more resistant from the less resistant components has been described by H. Jentgen[1] as follows: Ten grams of the air-dry cellulose of known dry weight are macerated and thoroughly stirred up to a uniform paste with 50 cc. of sodium hydroxide solution of 17.5% strength (sp. gr. 1.2) for exactly half an hour at the ordinary temperature. The mixture is then diluted with 50 cc. of water and the fluid is immediately poured on to a Buchner funnel with a fine cotton filter cloth. It is sucked as dry as possible with the pump and washed with successive quantities of 50 cc. each of water, draining thoroughly after each washing. The washed residue of resistant α-cellulose is soured with dilute acetic acid, then washed with hot water and dried in the oven and weighed. The alkaline filtrate and washings, amounting to about 1 liter, is acidified without delay with a slight excess of acetic acid and heated in the water-bath until the flocculent precipitate of gelatinous β-cellulose coagulates. This is then filtered off hot on a folded filter of fine cambric, washed with boiling water, scraped off the filter into a flat dish, dried at 100° C. and weighed. Only a minor portion generally of the less resistant cellulose is re-precipitated by acid in this manner and the remainder, calculated by difference, is classed as γ-cellulose, consisting mainly of components of the β-cellulose which have been hydrolyzed to permanently soluble products.

Pentosans. The pentosan ("furfuroid") groups present in commercial celluloses are estimated exactly in the same manner as that described for the raw materials. There appears to be no reason for regarding the pentosan groups of vegetable tissues in any other light than the other polysaccharides of the cellulose complex. Some belong to components of the "hemi-cellulose" type and are removed in the purification of the cellulose. Others are of the β-cellulose type and are to be accepted and valued as integral components of the commercial cellulose according to its species, while other members of the pentosan group are only

[1] Kunst. 1911, **1**, 165; Wag. Jahr. 1911, **57**, II, 426; Zts. ang. Chem. 1911, **24**, 1341.

slightly, if at all, less resistant than the α-cellulose itself. The proportion of pentosan groups remaining in the purified cellulose depends first on the species of raw material from which it was derived and secondly on the severity of the processes employed in its isolation. Thus, cellulose carefully prepared by the chlorination treatment in the laboratory will contain a more substantial portion of the original pentosan groups than cellulose of the same variety prepared commercially by manufacturing processes.

Alkaline Hydrolysis. Various modifications of Cross and Bevan's method of β-hydrolysis described under the section devoted to raw materials have been proposed and adopted in the examination of isolated and purified celluloses. It is obvious that some such test is desirable in the case of cellulose, but the interpretation of the results is far more difficult than in the case of raw materials. Any cellulose, even though it has been isolated by digestion with caustic soda will always yield a further quantity of soluble matter when it is again subjected to an alkaline treatment.

The loss of substance by hydrolysis of a commercial cellulose with boiling sodium hydroxide solution may fall under several heads: (1) The previous purification of the cellulose may have been defective and a portion of the loss in the alkaline hydrolysis test may be due to the further removal of original impurities. (2) The cellulose may be a variety which is rich in components of the β-cellulose or pentosan type and the hydrolysis by attrition of these less resistant groups may be continued almost indefinitely. (3) The previous industrial purification, if it be of an acid character as in the bisulfite process, may have modified even the α-cellulose so that it has become particularly susceptible to the attack of alkaline hydrolytic agencies. (4) If the cellulose has been bleached a similar susceptibility may have been induced by the oxidation of the fiber.

Thus the results of the test, as applied to purified and bleached cellulose may represent the sum of a number of complex factors, and it may be said that the function of this test is to call attention to the existence of certain divergences from type without, however, indicating the cause of such abnormalities.

The procedure adopted in the United States is based on some investigations made by E. Parker.[1] About 2 gm. of cellulose of known dry weight are covered with 100 cc. of a 10% solution of potassium hydroxide and the liquid is boiled for three hours without loss of water by evaporation, care being taken, however, to avoid local overheating and exposure of the cellulose above the surface of the liquid. At the end of the operation the cellulose is collected in a Gooch crucible, washed, soured, washed again and dried in the oven. The percentage loss of weight is calculated on the dry substance.

According to the modification of the test prescribed by the British War Office, 3 gm. of the cellulose, previously extracted with ether, are covered with 300 cc. of a 3% solution of sodium hydroxide and boiled gently for one hour, the manipulation being otherwise the same as described above.

Modified Cellulose. An important section of the analytical chemistry of cellulose is concerned with the determination of what may be called the "chemical condition" of cellulose. Interest in this aspect has grown up with the development of the chemical industries which employ purified cellulose as their raw material, as it became recognized that two specimens of cellulose of similar origin and purified apparently in a similar manner are not necessarily chemically equivalent.

Owing to its complexity cellulose is a very sensitive organism and its integrity is liable to modification by the cumulative effect of almost every agency to which it has been exposed. The analytical problem then is to determine in what sense and to what degree such modification has taken place. The results may be used for comparing a modified cellulose with a normal specimen of the same type in order to establish the optimum characteristic of the species, or else for comparing various types of cellulose with a standard type, for which cotton cellulose is adopted by general consent.

The chief modifications to be recognized are those due to hydration, oxidation, acid hydrolysis and "depolymerization."[2]

Hydrated Cellulose. It is recognized that cellulose is cap-

---

[1] J. Phys. Chem. 1913, **17**, 219; abst. C. A. 1913, **7**, 2302; J. C. S. 1913, **102**, i, 594; J. S. C. I. 1913, **32**, 419; Bull. Soc. Chim. 1913, **14**, 863; Chem. Zentr. 1913, **84**, I, 1727.

[2] J. Briggs, "Recent Progess in the Analysis of Cellulose and Cellulose Derivatives," Analyst, 1915, **40**, 114. A comprehensive and exhaustive résumé.

able of existing in various stages of colloidal activity which, in their relation to water, may be described as degrees of hydration, sometimes termed degrees of "mercerization." It was formerly held that cellulose formed loose combinations with water, constituting definite hydrates to which it was attempted to assign formulas in molecular terms. A distinction was made between hygroscopic moisture and water of hydration, which were supposed to be expelled at different temperatures corresponding to a difference in the nature of the union. These views, however, have been modified, and it is necessary now to regard the phenomenon of hygroscopicity merely as a manifestation of hydration, both belonging to the same order of adsorption phenomena common to the colloidal condition.[1] In the presence of an excess of moisture, whether in the form of atmospheric aqueous vapor or of liquid water, an adsorption equilibrium is set up between the cellulose and the surrounding medium, and the proportion of water fixed in the cellulose depends on its colloidal development. In this sense, all celluloses, including even the normal cotton cellulose, are hydrated, but the degree of hydration is capable of modification over a very wide range by chemical or mechanical treatments.

Thus hydration being a colloidal adsorption phenomenon, the degree of hydration may be measured analytically by estimating the relative adsorption capacity of the cellulose for various chemical substances under strictly standardized conditions.

Several tests of this nature have been described, one of the most useful qualitative indications being the blue adsorption compound which cellulose of a high degree of colloidal hydration forms with iodine. So-called vegetable parchment in which the cellulose has been converted into a colloid condition by the action of sulfuric acid gives the blue coloration directly with a solution of iodine in potassium iodide. Less modified forms of cellulose adsorb in a minor degree and a sensitizing agent must be added to the iodine solution before the blue stain can be developed. The sensitizing agent may be sulfuric acid or zinc chloride of a certain concentration or in general any liquid which has a vigorous hydrating action on cellulose. The test lends itself admirably to microscopic manipulation, and it may be utilized in two ways:

---

[1] Papierfabr. 1910 (Festheft), **8**, 46; abst. J. S. C. I. 1910, **29**, 874.

(1) With a constant concentration of the sensitizing agent, to identify those forms of cellulose which are more susceptible than others to the hydrating agencies, that is to say, those celluloses which already exist in a more highly hydrated condition will be stained blue by a reagent which will merely color the less hydrated modifications red. (2) With cellulose of any degree of hydration, to determine the concentration of sensitizing agent which is required to effect the transition from the red to the blue iodine coloration.

F. Vetillard[1] employs the iodine in a separate solution from the sensitizing agent and steeps the cellulose on a microscope slide in a drop of a saturated solution of iodine in 1% potassium iodide solution. The excess of iodine solution is absorbed with bibulous paper and the preparation is mounted in a sensitizing reagent consisting of a mixture of 3 parts by volume of concentrated sulfuric acid, 2 of glycerol and 1 of water.

W. Herzberg[2] prefers to use zinc chloride as a sensitizer, and combines the iodine in the same solution. Herzberg's reagent is made with 20 gm. of zinc chloride dissolved in 10 gm. of water, and this solution is then mixed with a solution made up with 2.1 gm. of potassium iodide, 0.1 gm. of iodine and 5 gm. of water.

J. Hübner[3] describes various methods of applying the iodine-zinc chloride reagent at different concentrations in order to ascertain the degree of hydration (mercerization) of a fibrous cellulose, all of which are based on the development of the blue adsorption compound with more or less ease according to the initial degree of hydration existing. Thus it is possible to determine with certainty whether a given sample of cotton has been mercerized or not, and it is possible, within certain limits, to determine with what concentration of alkali the mercerizing effect was produced.

E. Knecht[4] has devized a method having a similar object, based on the increased adsorption of substantive dyestuffs by

---

[1] "Etudes sur les Fibres textiles," 1876, 28, 29.

[2] "Papierprüfung," Berlin, 1902, p. 65.

[3] J. S. C. I. 1908, **27**, 105; Proc. Manch. Lit. Phil. Soc. 1908, **52**, 2; abst. C. A. 1908, **2**, 1187, 1347; Chem. News, 1908, **97**, 10; Proc. Chem. Soc. 1907, **23**, 304; Bull. Soc. Chim. 1908, **4**, 1660; Rep. Chim. 1908, **8**, 238; Chem. Zentr. 1908, **79**, I, 1097; Chem. Ztg. 1908, **32**, 220; Jahr. Chem. 1905–1908, II, 3185; Meyer Jahr. Chem. 1908, **18**, 505; Wag. Jahr. 1908, **54**, II, 467; Zts. ang. Chem. 1908, **21**, 87, 1760.

[4] J. Soc. Dyers Col. 1908, **24**, 67; J. S. C. I. 1908, **27**, 400; abst. Chem. Ztg. Rep. 1908, **32**, 272; Wag. Jahr. 1908, **54**, II, 467.

hydrated cellulose, the cellulose to be examined being dyed, together with a standard sample of cellulose, in the same bath of Benzopurpurin 4-B. After the dyeing, the depth of the shades may be compared and the relative amounts of dyestuffs fixed on the fibers may be estimated by titration with titanous chloride.

C. Schwalbe[1] also uses an adsorption method to give what he calls the hydration copper value of the cellulose which is based on the relative quantity of cupric hydroxide adsorbed by the cellulose from Fehling's solution in the cold.

W. Vieweg[2] proposes for the same purpose to measure the adsorption of caustic soda by dry cellulose from a 2% solution of sodium hydroxide under standard conditions and J. Briggs[3] has shown that the adsorption of sodium hydroxide from a solution in 93% alcohol takes place on a magnified scale and that a simple and convenient method for estimating the degree of hydration, however, produced, may be based empirically on the adsorption of alkali from a 2% solution of sodium hydroxide in 93% alcohol at the ordinary temperature.

A method based on the rate of hydrolysis with boiling dilute sulfuric acid was proposed by C. Schwalbe,[4] but it cannot be admitted that the hydrolysis value so found stands in a sufficiently direct relation to the degree of hydration as generally understood.

A hydrated cellulose parts with the whole of its water of hydration when heated above 100° C., for instance, up to 120° C., and then acquires the composition of anhydrous cellulose corresponding to the empirical formula $C_6H_{10}O_5$. The colloidal condition or structure on which its degree of hydration depends is only partially affected by such temporary dehydration. On reexposure the cellulose still shows the characters imparted to it by its hydration, though in a modified degree, and does not re-

---

[1] "Die Chemie der Cellulose," Berlin, 1911, p. 634.

[2] Chem. Ztg. 1908, **32**, 329; Zts. ang. Chem. 1908, **21**, 87, 865; abst. C. A. 1908, **2**, 1883; J. S. C. I. 1908, **27**, 418; Bull. Soc. Chim. 1908, **4**, 1467; Chem. Zentr. 1908, **79**, I, 1617, 2025; Wag. Jahr. 1908, **54**, II, 493.

[3] Chem. Ztg. 1910, **34**, 455; abst. C. A. 1910, **4**, 2372; J. S. C. I. 1910, **29**, 622; Bull. Soc. Chim. 1911, **10**, 60; Chem. Zentr. 1910, **81**, I, 2075; Jahr. Chem. 1910, **63**, II, 422; Zts. ang. Chem. 1910, **23**, 1389; Zts. Chem. Ind. Koll. 1911, **8**, 57.

[4] Zts. ang. Chem. 1908, **21**, 400, 401, 1321, 2311; abst. C. A. 1908, **2**, 1885, 2448; 1909, **3**, 406; J. C. S. 1908, **94**, ii, 627; J. S. C. I. 1908, **27**, 294; Bull. Soc. Chim. 1908, **4**, 633; 1909, **6**, 58; Chem. Zentr. 1908, **79**, I, 1336; II, 447; Jahr. Chem. 1905–1908, II, 960; Meyer Jahr. Chem. 1908, **18**, 504; Wag. Jahr. 1908, **54**, II, 492.

turn to its original condition. For instance, mercerized cotton is characterized by a strongly increased adsorption capacity for substantive dyestuffs. If the cotton, after being mercerized, be dried by heat before dyeing, the adsorption capacity is distinctly less than if it be dyed directly after mercerizing, but it is always considerably greater than that of the original unmercerized cotton. In quantitative tests, therefore, it is not a matter of indifference whether the cellulose to be tested be dried in the oven or not, and a standard procedure in this respect must be adopted.

Oxycellulose and Hydrocellulose. Cellulose modified by oxidizing agents of hydrolyzing acids acquires cupric reducing properties owing to the formation or opening up of free carbonyl groups. Neither oxycellulose nor hydrocellulose can be described in terms of definite compounds; they merely indicate the sense in which the cellulose complex has suffered modification, in degrees which appear capable of infinite variation.

Oxycellulose and hydrocellulose must be assumed to differ in the mode of formation of the open carbonyl groups which characterize them. In the case of oxycellulose there appears to be a definite oxidation of alcoholic hydroxyls into aldehydic carbonyl radicals, such an action being equivalent to an increase in the balance of acidity in the groups of the cellulose complex. In the case of hydrocellulose no such acidification takes place and an analogy may be drawn with the hydrolytic fission which takes place in the hydrolysis of starch and other polysaccharides with the formation of cupric-reducing dextrins.

Estimation of Copper Value. The degree of modification in either sense is measured by estimating the cupric-reducing value of the celluloses with Fehling's solution, the "copper value" being calculated as the number of grams of copper reduced from Fehling's solution by 100 gm. of cellulose. The method has been standardized by C. Schwalbe,[1] who investigated very thoroughly the numerous sources of error which make it somewhat difficult to obtain strictly comparable results. The purity of the chem-

---

[1] "Die Chemie der Cellulose," p. 625. Zts. ang. Chem. 1910, **23**, 924; abst. C. A. 1912, **6**, 159; J. S. C. I. 1910, **29**, 689; Bull. Soc. Chim. 1910, **8**, 943; Chem. Zentr. 1910, **81**, II, 339; Chem. Ztg. Rep. 1910, **34**, 335; Jahr. Chem. 1910, **63**, II, 1135; Wag. Jahr. 1910, **56**, 499. Zts. ang. Chem. 1914, **27**, 567; abst. C. A. 1915, **9**, 712; J. S. C. I. 1915, **34**, 23; Wag. Jahr. 1914, **60**, II, 408. Ber. 1907, **40**, 1347; abst. Chem. Zentr. 1907, **78**, I, 1490.

icals used for making up the Fehling's solution must be carefully controlled and contact with rubber or cork stoppers and other organic matters, including filter paper, must be avoided from start to finish. The flask in which the cellulose is boiled with the Fehling's solution is provided with a surface-condenser suspended in the neck and the glass shaft of a mechanical stirring apparatus passes through the center of the condenser. A weighed quantity of the air-dry cellulose equivalent to 2–3 gm. of dry substance is placed in the boiling flask with 250 cc. of water and the liquid is heated to the boil while stirring continuously. Meanwhile, 50 cc. each of Fehling's copper sulfate and alkaline tartrate solutions are separately heated to boiling, mixed at the boil and added to the boiling water and cellulose in the flask, using 50 cc. of boiling water to rinse the vessels. When the total mixture has again come to the boil it is boiled for exactly fifteen minutes. The flask is quickly removed and about 1 gm. of kieselguhr suspended in water is added and shaken round in order to coagulate any finely suspended cuprous oxide. The cellulose is then rapidly filtered off on a Buchner funnel with double paper filter and thoroughly washed with boiling water. The cuprous oxide deposited in the cellulose and on the filter is dissolved in nitric acid and estimated by the electrolytic method. It is extremely important, during the boiling, to keep the cellulose constantly stirred and completely submerged in the boiling liquid. The electrolytic determination of the copper is somewhat inconvenient in a technical laboratory; moreover, cupric hydroxide is deposited by adsorption on the cellulose together with the cuprous oxide and cannot be washed out. A more convenient and rapid method whereby the cuprous oxide alone is determined by titration has been indicated by E. Hägglund,[1] and consists in treating the cellulose on the filter with 100 cc. of a boiling solution of ferric sulfate strongly acidified with sulfuric acid. This solution contains 50 gm. of ferric sulfate and 200 gm. of sulfuric acid per liter, and is previously freed from any ferrous salt by adjustment with permanganate. The cuprous oxide is immediately dissolved and reduces an equivalent amount of ferric salt to the ferrous condition, the quantity thus reduced being titrated in the filtrate.

[1] Papierfabr. 1919, **17**, 301; abst. Chem. Zentr. 1919, **90**, IV, 296; J. S. C. I. 1919, **38**, 894-A; C. A. 1919, **13**, 3009.

The following copper values have been quoted by Schwalbe for various specimens:

Surgical cotton wool	1.64 to 1.8
Mercerized bleached Egyptian cotton	0.9 to 1.6
"Glanzstoff" artificial silk	1.1
Hydrocellulose up to	5.2 to 5.8
Parchment paper	4.2
Bleached sulfite wood-pulp	3.9
Oxycellulose may show any number up to about	16.0

Schwalbe's complete prescription is so complex that many attempts have been made to simplify its details; nevertheless, it must be conceded that all the precautions which he prescribes are well founded in fact.

The following procedure has been adopted for technical purposes by the British War Office: 12.5 cc. each of Fehling's copper sulfate and alkaline tartrate solutions[1] are mixed in a conical flask fitted with an air condenser and the liquid is heated for five minutes in a boiling water-bath. If the solution shows no spontaneous precipitation of cuprous oxide it is considered to be good, and 50 cc. of boiling water and 1 gm. of cellulose are added. The flask is again heated for 15 minutes in the boiling water-bath, the contents are then immediately filtered off on a Buchner funnel. The cellulose is washed with boiling water, then with a 10% solution of Rochelle salt and lastly with boiling water. The whole is incinerated, the copper oxide is dissolved in nitric acid and estimated volumetrically by the iodide method. Here again it may be remarked that the ferric sulfate method is greatly to be preferred both for simplicity and accuracy. It must be noted that copper values determined by boiling for 15 minutes are never to be compared with those determined by heating in the boiling water-bath for the same length of time. The effect of the numerous sources of error is much smaller in the latter method, but at the same time the copper values themselves are also very much lower. It should also be noted that according to the English method the copper values are calculated in terms of cuprous oxide and not of metallic copper.

The estimation of the copper value is the most definite measure for the diagnosis of the chemical condition of the cellulose in

---

[1] The Fehlings copper solution contains 69.28 gm. of crystallized pure copper sulfate and 1 cc. of pure sulfuric acid in one liter. The Alkaline Tartrate solution contains 350 gm. of Rochelle salt and 100 gm. of sodium hydroxide in one liter.

numerical terms which is available. The purest bleached cotton of the highest commercial quality shows a copper value considerably less than 1, but commercial specimens with copper values between 1 and 2 are fairly common. The latter values already indicate a distinct amount of chemical modification of the cellulose as the result of injudicious bleaching, although this modification may not have gone so far as perceptibly to lower the tensile strength. With more profound modification the copper value increases and a rapid loss of tensile strength and durability of the fiber is observed. Nevertheless, the absolute value of the cupric-reducing power is not a direct measure of the loss of quality, and a given degree of structural disintegration in the sense of hydrocellulose will correspond with a far lower copper value than a similar degree of modification in the sense of oxycellulose. Moreover, structural weakness may be induced by agencies which do not develop a corresponding increase in the copper value, for instance, excessive boiling with caustic soda lyes or exposure to dry heat to the point of scorching. It is necessary, therefore, to pay attention to other diagnostic details before a complete account can be given of chemically modified celluloses.

For the distinction between oxycellulose and hydrocellulose the copper value does not suffice, and it is necessary to have recourse to qualitative tests.

As was remarked before, these modifications of cellulose are characterized by free carbonyl groups which are probably different in origin. In both cases the carbonyl groups are soluble in boiling caustic soda solution with the formation of yellow products. In the case of oxycellulose, however, the products formed with boiling dilute (normal) sodium hydroxide are characterized by a transient intensely golden yellow color, which subsequently diminishes and becomes brownish in shade. In the case of hydrocellulose the coloration is less intense and brownish yellow from the beginning. Boiling sodium hydroxide gradually hydrolyzes and dissolves the carbonyl groups of these modified celluloses so that the copper value of the residue after treatment is considerably lowered and possibly reduced to normal proportions. The tensile strength, however, is not restored and the residue cannot be described as normal cellulose, although substantially free from cupric-reducing groups. Such modified and subsequently treated cellulose is characterized by its very low viscosity (see below). Oxycellulose may also be differentiated from hydrocellulose in the fact before mentioned, that the oxidation of certain groups disturbs the balance of basic and acidic hydroxyls and increases the acidity of the cellulose molecule. This increased acidity of the oxidized cellulose confers on it the property of increased affinity for dyestuff bases, so that basic dyestuffs are more readily fixed on the oxidized fiber than on the normal fiber, whereas hydrocellulose possesses no such increased affinity. This property forms the basis of the methylene blue test for oxycellulose which, however, since it depends on a contrast of colors, can only be of service when the oxidation of the fiber is localized.[1]

Viscosity. The viscosity of solutions of fully purified cellulose is held to be a measure of the chemical quality of the cellulose in the sense that solutions of modified celluloses are extremely deficient in "body." The relation between viscosity and quality has long been recognized in the artificial silk industry, but it holds good only within restricted limits and with many reservations. In the manufacture of viscose it is established that the viscosity of the xanthate varies with every chemical modification which the cellulose has undergone; nevertheless, chemical quality is only one of the factors which influence viscosity, and the relations of the cellulose to the solvent is certainly another factor. Hence in comparing viscosities it is important that the composition of the solvent be absolutely constant and that the purity of the cellulose be complete; the presence of small residues of lignin, by affecting the solubility, makes the test unsatisfactory.

The viscosity test in cuprammonium solution was first described as a quantitative method by H. Ost,[2] and has subsequently been investigated and developed by the research department of the British War Office at Woolwich into a standard test by which the chemical quality of a purified cellulose may be numerically recorded.

The greatest care must be taken in making up the cuprammonium solvent in order to have a liquid of constant comparison and free from salts. The reagent is prepared from carefully pre-

---

[1] J. Briggs, J. S. C. I. 1916, **35**, 79; abst. C. A. 1916, **10**, 1098.

[2] Zts. ang. Chem. 1911, **24**, 1892; abst. C. A. 1912, **6**, 684; J. C. S. 1911, **100**, i, 838; J. S. C. I. 1911, **30**, 1247; Chem. Zentr. 1911, **82**, II, 1518; Chem. Ztg. Rep. 1911, **35**, 520; Wag. Jahr. 1911, **57**, II, 428.

cipitated and thoroughly washed cupric hydroxide, free from basic copper sulfate, dissolved in concentrated ammonia solution. The composition must be checked by analysis and the solution must show copper (as Cu) equal to 10 gm. per liter within 0.15 gm. on either side. According to another prescription the cuprammonium reagent must contain 12 gm. per liter of copper. The ammoniacal strength of the solution determined by distillation must be 200 gm. of NH_3 per liter, within 5.0 gm. on either side.

In preparing and manipulating the solution of cellulose in this reagent every precaution must be taken to protect the solution from the action of light and air, as these cause a rapid lowering of the viscosity owing to the oxidation of the dissolved cellulose. For this purpose the air must be completely evacuated from the bottle in which the solution of cellulose is prepared as soon as the cellulose and cuprammonium reagent have been introduced.

A quantity of air-dry cellulose, previously extracted with ether if necessary, equivalent to exactly 2 gm. dry weight is introduced into 100 cc. of the reagent contained in a stout glass bottle of 150 cc. capacity from which the air is then immediately evacuated. The contents of the bottle, including a few glass beads, are then shaken until the cellulose is finally dissolved. The bottle is then fitted with another rubber stopper through which pass two glass tubes, one to the bottom of the bottle and the other only through the cork. The latter is adapted to reach to the bottom of a standard straight viscosimeter tube and when the bottle is inverted the transference of the cellulose solution to the viscosimeter is effected with a minimum exposure of the liquid to the air and without agitation. The viscosimeter tube, closed at the bottom, has a total length of 30 cm. and an internal diameter of 1 cm.; it is divided by graduations exactly 5 cm. apart and must be filled to within 3 cm. of the top. It is kept in a dark box in which the temperature is maintained constant at 20° C. Steel balls, $^1/_{16}$ in. in diameter, are introduced through a special releasing tube which passes through a rubber cork in the mouth of the viscosimeter tube and the time of fall through a path of 15 cm. indicated by the graduation marks is noted by means of a chronometer.

The absolute viscosity of the cellulose solution may be calculated in C. G. S. units by a modification of Stokes' formula worked out by S. Sheppard,[1] which corrects for the retardation due to the walls of the viscosimeter tube. A simpler procedure is to work with standardized viscosimeter tubes which have been calibrated with pure castor oil, the absolute viscosity of which is known ($\eta' = 9.65$ Woolwich standard). The viscosity of the

---

1. J. Ind. Eng. Chem. 1917, **9**, 523; abst. C. A. 1917, **11**, 114, 1778; J. C. S. 1917, **112**, ii, 359; J. S. C. I. 1917, **36**, 670. S. Zeisel and M. Stritar (Ber. 1902, **35**, 1252; abst. J. S. C. I. 1902, **21**, 642) have described the following method for the determination of cellulose.

In the presence of nitric acid the non-cellulose of wood is oxidized rapidly by potassium permanganate in the cold, and completely converted into products soluble in dilute ammonia. It is true that in this, as in all oxidation processes, a large portion of the cellulose—about 30%—7 is also converted into oxycellulose, which is insoluble in the above solvent, but which may be extracted by boiling with 10% soda lye. The error thus involved is quite small, but it can be estimated by extraction and allowed for. At the same time, this and other oxidation processes are accompanied by the conversion of some of the cellulose—at most 4%—into soluble products. The estimation is carried out as follows: About 1–1.5 gm. of the crude, finely divided substance (e. g., oak-wood raspings) is macerated with dilute nitric acid, and a 3% solution of permanganate is run in, 1 cc. at a time, stirring, and cooling, until the red color persists for half an hour. This operation occupies about two hours; the excess of permanganate and the precipitated oxide are removed by sulfurous acid, and the residue is filtered off, washed, and then treated for 45 minutes at 60° C. with a 2.5% solution of ammonia, being finally washed with water, alcohol and ether. The results agree very well with those which it requires 15 days to obtain by the Schulze-Henneberg process—extraction of the wood with water and alcohol, and prolonged oxidation with potassium chlorate dissolved in nitric acid. The yield of cellulose from oak-wood amounted to 37.2%, the product containing 0.5% of methoxyl. Experiments made with Schulze's original chlorate process invariably gave very much higher yields, but the presence of 5% or more of methoxyl in the cellulose obtained, indicated that the conversion was far from complete.

The author's researches also show that the hemicelluloses, particularly the mannoso-cellulose of the ivory nut, are completely converted into soluble products by permanganate, which is not the case with chlorate mixtures. This process, therefore, is adapted for the direct estimation of cellulose in its narrower sense, i. e., the dextroso-celluloses. See also Ann. Chim. anal. **8**, 77; abst. Bied. Centr. 1902, **31**, 863; J. S. C. I. 1903, **22**, 321. For additional information on this subject, consult, C. Cross and E. Bevan, Zts. Farbenind. 1912, **11**, 197; abst. J. C. S. 1912, **102**, ii, 1105. Eighth Intl. Cong. Appl. Chem. 1912, **13**, 101; abst. J. S. C. I. 1912, **31**, 870. R. Dmochowski and B. Tollens, J. Landw. 1910, **58**, 21; abst. J. C. S. 1910, **98**, ii, 555. A. Gregoire and E. Carpiaux, Bull. Soc. Chim. Belge, 1910, **24**, 217; abst. J. C. S. 1910, **98**, ii, 661. P. Klason, Chem. Ztg. 1903, **27**, 585; abst. J. S. C. I. 1903, **22**, 826. J. König, Zts. Nahr. u. Genussm. 1903, **6**, 769; abst. J. C. S. 1903, **84**, ii, 764. Zts. Nahr. u. Genussm. 1906, **12**, 385; abst. J. C. S. 1906, **90**, ii, 905. Ber. 1908, **41**, 46; abst. J. C. S. 1908, **94**, ii, 236. J. König and F. Hühn, Zts. Farbenind. 1911, **10**, 297, 326, 344, 366; 1912, **11**, 4, 17, 37, 57, 77, 102, 209; abst. J. C. S. 1912, **102**, ii, 1005. H. Matthes, Ber. 1908, **41**, 400; abst. J. C. S. 1908, **94**, ii, 236. O. Simon and H. Lohrisch, Zts. physiol. Chem. 1904, **42**, 55; abst. J. C. S. 1904, **86**, ii, 787.

cellulose solution is then calculated by the simple proportional formula

$$\frac{\eta}{\eta'} = \frac{T(S - S')}{T'(S - S'_1)}$$

in which η is the absolute viscosity of the cellulose solution

η' is the absolute viscosity of castor oil

T is the time of fall in the solution

T′ is the time of fall in castor oil

S is the density of the steel ball (7.65)

S′ is the density of the cellulose solution

S'_1 is the density of castor oil (0.96).

The method gives fairly satisfactory results with duplicate determinations if the conditions are rigidly maintained, but the interpretation of them must be made with some caution. In the case of high viscosities the differences between similar samples of cellulose may be extraordinarily great, while in the case of low viscosities considerable differences between two samples of cellulose may be recognized by other methods without any sufficiently perceptible difference in viscosity. Thus, in the case of cellulose modified by hydrolysis or oxidation, the viscosity values are uniformly extremely low, but the different degrees of modification such as would be recognizable easily by tensile tests or cupric reducing values, are barely indicated by the viscosity test.

On the other hand, the viscosity method is often the only test which will indicate modification of cellulose which has been brought about in such a way that the product does not reduce Fehling's solution; for instance, cellulose which has been modified by prolonged dry heating above 100° C., cellulose which has been modified by the action of caustic soda at excessively high temperatures in the purification process, or oxycellulose and hydrocellulose from which the cupric-reducing, free carbonyl groups have been largely or wholly removed by digestion with caustic alkalis. All these forms of modified cellulose, when the modification has not proceeded far enough visibly to affect their tensile strength may be revealed by their abnormally low viscosity values.

It may reasonably be inferred that with certain reservations a relationship exists between the viscosity of the solutions, the state of polymerization of the cellulose, and its tensile strength, but the conditions of the relationship have never been systematically worked out.

CHAPTER II.

STARCH.

Origin and Transformations of Starch.[1] Starch has, as yet, not been prepared artificially, and but little progress has been made in this direction notwithstanding the multiplicity of investigators who have engaged themselves with this problem.

Chlorophyl, which plays such an essential part in the characteristic function of "assimilation" in all green plants, i. e., the ab-

---

[1] For general information on the subject of starch, see C. O'Sullivan, J. Chem. Soc. 1886, 70; Chem. News, 1885, **52**, 293. E. Schulze and Frankfort, Ber. 1894, **28**, 64. Naegeli, Die Staerkekoerner, 1858, 378, 535. Burgerstein, Ber. bot. Ges. 1900, **18**, 180. J. Thresh, Pharm. J. Transact. 1884, 798. Weizmann, Arch. Pharm. 1886, 909. A. Petermann, Centr. Agr.-chem. 1878, 869. Balland, Just. Jahr. 1897, II, 85. Sudakoff, Just. Jahr. 1879, I, 399. G. Baumert and K. Halpern, Arch. Pharm. 1893, **231**, 641. Pellett and Liebschutz, Compt. rend. 1880, **90**, 1363. Loebe, Jahr. Agr.-chem. 1890, 443. Lehmann and Mori, Arch. Hyg. 1889, 257. Meissl and Boecker, Monatsh. Chem. 1883, **4**, 349. J. Moser, Centr. Agr. chem. 1879, 388. Balland, Compt. rend. 1901, **132**, 1061. L. Jahne, Centr. Agric. chem. 1881, 106. Hannamann, Jahr. 1885, I, 75. Chodat and Chuit, Just Jahr. 1888, I, 57. Beckurts, Arch. Pharm. 1894, **231**, 687. C. Hopkins, Smith and East, J. Amer. Chem. Soc. 1903, **23**, 1166. C. Brisseau-Mirbel, Elemens de phys. veget, 1815, I, 185. Raspail, Annal. scien. nat., March 1826; Mem. soc. d'hist. nat. 1827, **3**, 17. Caventou, Ann. Chim. Phys. 1826, (2), **31**, 337. Guibort, Ann. Chim. Phys. 1829, (2), **40**, 183. R. Guerin-Varry, Compt. rend. 1836, **2**, 116; Ann. Chim. Phys. 1836, (2), **41**, 66. Candolle, Physiologie. deutsch v. Roeper, 1833, **1**, 149. J. Fritzsche, Pogg. Ann. 1834, **32**, 129; Ann. 1836, **37**, 114. Biot, Compt. rend. 1844, **18**, 795. Ehrenberg, J. prakt. Chem. 1850, **49**, 490. Marcet, Ann. Chim. Phys. 1827, (2), **36**, 27. Payen, Compt. rend. 1836, **3**, 224; Ann. Chim. Phys. 1836, (2), **61**, 355; 1837, (2), **45**, 255; Annal. sci. nat. 1838, 5. Colin and G. de Claubry, Schw. Jour. 1815, **13**, 453. Strohmeyer, Gilb. Ann. 1815, **49**, 146. Nasse, Schw. Jour. 1812, **4**, 111. J. Schrader, Schw. Jour. 1812, **4**, 108. Vogel, Gilb. Ann. 1812, **42**, 125; Schw. Jour. 1812, **5**, 80. Gehlen, Schw. Jour. 1812, **5**, 32. Davy, Elem. d. Agrikult. Chem. 1814, 146. T. Saussure, Gilb. Ann. 1815, **49**, 129; Schw. Jour. 1819, **27**, 323. Braconnot, Ann. Chim. Phys. 1833, (2), **52**, 290. Biot and Persoz, Ann. Chim. Phys. 1833, (2), **52**, 72. Payen and Persoz, Ann. Chim. Phys. 1833, **53**, 73; 1835, **60**, 441. A. Meyer, Untersuchungen ueber die Staerkekoerner, 1895, 78–79. A. Fernbach, Compt. rend. 1904, **138**, 428. Naegeli, Die Staerkekoerner, 1858; Botan. Zts. 1881, 633. A. Schimper, Botan. Zts. 1880, 881; 1881, 185. A. Meyer, Botan. Zts. 1881, 841. A. Dodel, Flora, 1892, 267. A. Binz, Flora, 1892, 34. Belzung, Annal. sci. nat. 1891, (7), **13**, 1. Koningberger, Botan. Centr. 1892, **49**, 47. C. Acqua, Malpighia, 1893, **7**, 393. J. Salter, Jahr. wissen. Botan. 1898, **32**, 127. L. Buscalioni, Nuov. Giorn. bot. Ital. 1891, **23**, 45; Just Jahr. 1891, I, 489. H. Fischer, Botan. Centr. 1902, B, **12**, 226; Ber. botan. Ges. 1903,

sorption of carbon dioxide from the air and its decomposition in the chlorophyl corpuscles with the evolution of oxygen, was in-

21, 107. Meyer, Botan. Ztg. 1881, 844. H. Fischer, Cohns. Beitr. z. Biolog. 1898, **8,** 79. Ber. botan. Ges. 1903, **22,** 107. H. Kraemer, Botan. Gaz. 1902, **34.** O. Buetschli, Verhandl. natur-med. Verein, Heidelb. 1893, **5,** 89; Botan. Centr. **56,** 150; Naturw. Rundsch. 1893, **8,** 357; Verhandl. Heidelberg, 1897, **5,** 457; Botan. Centr. 1896, **68,** 213. H. Rodewald and A. Kattein, Zts. physik. Chem. 1900, **33,** 579; Berl. Akad. 1899, **24,** 62. C. Scheibler, Ber. 1869, **2,** 170. Rodenwald, Landw. Versuchst, 1895, **45,** 201; Zts. physik. Chem. 1900, **33,** 540, 593. Rothert, Ber. botan. Ges. 1897, **15,** 234. E. Ott, Oesterr. botan. Zeits. 1899, **39,** 313. S. Schubert, Monatsh. Chem. 1884, **5,** 472. Hoppe-Seyler, Ber. 1870, **4,** 15. Lippmann, J. prakt. Chem. 1861, **83,** 51. V. Syniewski, Ann. 1899, **309,** 282. Ambronn, Ber. saechs Ges. d. Wiss, 1891, 28. Mauch, Chem. Centr. 1902, **73,** I, 1199. F. Musset, Chem. Centr. 1896, **67,** 703. Tollens, J. Landwirtsch. 1873, 375. A. v. Asboth, Chem. Ztg. 1887, **11,** 147; Jahr. Agri. Chem. 1887, 406; Ber. 1888, **21,** 454. C. Lintner, Zts. ang. Chem. 1888, **1,** 232. Zulkowski, Ber. 1880, **13,** 1398; 1890, **23,** 3295. Lassaigne, Ann. Chim. Phys. 1833, (2), **53,** 109. Leroy and Raspail, Schw. Jour. 1833, **68,** 179. H. Stokes, Chem. News, 1887, **56,** 112. Meineke, Chem. Ztg. 1894, **18,** 157. E. Schaer, Pharm. Centralh. 1896, **37,** 540. E. Heintz, Jahr. Agr. Chem. 1879, 499. E. Puchot, Ber. 1876, **9,** 1472. J. Gruess, Jahr. wissen. Botan. 1896, **26,** 379. C. Roberts, Chem. Centr. 1894, **65,** II, 147. Mylius, Ber. 1887, **20,** 688. F. Hale, Amer. Chem. J. 1902, **28,** 438. C. Lonnes, Zts. anal. Chem. 1894, **23,** 409. F. Kuester, Ann. 1894, **283,** 360; Ber. 1895, **28,** I, 783. C. Meineke, Chem. Ztg. 1894, **18,** 157; Chem. Centr. 1894, **65,** I, 525. Mylius, Zts. physiol. Chem. 1887, **11,** 306; Ber. 1895, **28,** 385. E. Rouvier, Compt. rend. 1892, **114,** 128, 749; 1893, **117,** 281, 461; 1894, **118,** 743; 1895, **120,** 1179; 1897, **124,** 565. F. Seyfert, Zts. ang. Chem. 1888, **1,** 15. H. Stokes, Chem. News, 1887, **56,** 212; 1888, **57,** 183. F. Musset, Pharm. Centralh. 1896, **37,** 556. E. Sonstadt, Chem. News, 1873, **28,** 248. Pellet, Mon. Sci. 1877, **7,** 988. Bondonneau, Compt. rend. 1877, **85,** 671. C. Harz, Chem. Centr. 1898, **69,** I, 1018. Roberts, Chem. Centr. 1894, **65,** II, 147. H. Friedenthal, Centr. Physiol. 1899, **13,** 55. Andrews and Goettsch, Chem. Centr. 1902, **73,** II, 1035. G. Kruess and E. Thiele, Zts. anorg. Chem. 1894, **7,** 52. A. Lachman, J. Amer. Chem. Soc. 1903, **25,** 50. H. Beckurts and W. Freytag, Pharm. Centralh. 1886, **27,** 231. A. Michael, Amer. Chem. J. 1884, **5,** 359. Z. Skraup, Ber. 1899, **32,** II, 2413. F. Pregl, Sitzber. Wien. Akad. 1902, IIb, 881. Syniewski, Chem. Centr. 1902, **73,** II, 986. C. J. Lintner, Zts. ang. Chem. 1890, **3,** 546. J. Habermann, Ann. 1874, **172,** 11. A. v. Asboth, Chem. Centr. 1892, **63,** II, 867. W. Syniewski, Ber. 1897, **30,** 2415; 1898, **31,** 1791. A. Gris, Bull. soc. Bot. 1860, **7,** 876. A. Meyer, Arch. Pharm. 1883, **21,** No. 7–8; Ber. Deut. Bot. Ges. 1886, **4,** 337; 1887, **5,** 171. E. Russow, Sitz. Ber. Dorpater Naturforsch-Ges. 1884, **7,** P, 1. U. Kreusler and F. Dafert, Landw. Jahr. 1884, **13,** 767. Dafert, Landw. Jahr. 1886, **15,** 259; Sitzber. Niederrhein. Ges. Bonn, 1885, 337; Ber. Deut. Bot. Ges. 1887, **5,** 108. A. Beutell and Dafert, Chem. Ztg. 1887, **11,** 136. A. Tschirch, Ber. Deut. Bot. Ges. 1888, **6,** 138. C. Overhage, Just Jahr. 1888, I, 745. Y. Shimoyama, Dissert. Strassburg, 1886; Just Jahr. 1866, II, 315; Botan. Centr. 1887, **32,** 6. Pellet, Compt. rend. 1880, **90,** 1293. Levallois, Compt. rend. 1881, **93,** 281. Saito, Bot. Centr. 1901, **88,** 125. H. v. Mohl, Bot. Ztg. 1859, 225. Naegeli, Botan. Mitteil, 1863, 387, 415. A. Meyer, Bot. Ztg. 1886, 697. H. Brown and J. Heron, Ann. 1879, **199,** 165. C. O'Sullivan, Pharm. J. Trans. 1881, **12,** 451. H. de Vries, Just Jahr. 1885, I, 122. V. Syniewski, Ann. 1899, **309,** 282. E. Bourquelot, Compt. rend. 1887, **104,** 71, 177. Lintner, J. prakt. Chem. 1886, **34,** 378. J. Ford, Chem. Centr. 1904, **75,** II, 645. H. Ost, Chem. Ztg. 1895, **19,** 1501. A. Wrowlewski, Ber.

vestigated as far back as 1690 by de la Hire,[1] followed by Bonnet,[2] Priestly,[3] Senebier,[4] de Saussure,[5] and H. von Mohl;[6] the latter

---

1897, **30**, II, 2108; Chem. Ztg. 1898, **22**, 375. K. Zulkowski, Ber. 1880, **13**, 1398. V. Syniewski, Ber. 1897, **30**, 2415; 1898, **31**, 1791. F. Schulze, J. prakt. Chem. 1848, **44**, 178. L. Bondonneau, Ber. 1875, **8**, 438; Compt. rend. 1875, **80**, 671; **81**, 972, 1210. Beijerinck, Centr. Bakt. 1896, II, 697. Musculus, Compt. rend. 1870, **70**, 857; Ber. 1870, **3**, 430; 1874, **7**, 824; Bull. Soc. Chim. 1874, **22**, 26. W. Naegeli, Ann. 1874, **173**, 218. Bruecke, Sitzungsber. Wien. Akad. 1872, **45**, Abt. 3. Lintner and Duell, Ber. 1893, **26**, 2533; 1895, **28**, 1522. F. Salomon, J. prakt. Chem. 1883, **28**, 82. L. Schulze, J. prakt. Chem. 1883, **28**, 311. C. Schiebler and H. Mittelmeier, Ber. 1890, **23**, 3060. Ost, Chem. Ztg. 1895, **19**, 1500. F. Allihn, Zts. f. Ruebenzuckerind. 1883, 50. F. Allihn, J. prakt. Chem. 1880, **22**, 46. G. Rolfe and Defren, J. Amer. Chem. Soc. 1896, **18**, 869. C. Lintner and G. Duell, Ber. 1895, **28**, 12. Flourens, Compt. rend. 1890, **110**, 1204. Musculus, J. prakt. Chem. 1883, **28**, 496. J. Effront, Mon. Sci. 1887, **29**, 513. G. Rolfe and H. Geromanos, J. Amer. Chem. Soc. 1903, **25**, 1003, 1015. H. Dierssen, Zts. ang. Chem. 1903, **16**, 121. C. Lintner, Chem. Ztg. 1897, **21**, 737. R. Young, J. Physiol. 1898, **22**, 401. Zulkowski, Chem. Centr. 1888, **59**, II, 1060. Zulkowski and B. Franz, Oestrr. Gess. Forder. Chem. Ind. **16**, 120; abst. Chem. Centr. 1894, **65**, II, 918; Jahr. f. Agrik. Chem. 1895, 633. H. Friedenthal, Centr. Physiol. 1899, **12**, 849. Pfeiffer and Tollens, Ann. 1881, **210**, 295. Mylius, Ber. 1887, **20**, 694. F. Salomon, J. prakt. Chem. 1882, **25**, 348; 1882, **26**, 324; 1883, **28**, 82. R. Sachsse, Sitzungsber, Naturforsch. Ges. Leipzig, 1877, **4**, 30. H. Rodewald, Zts. physik. Chem. 1900, **33**, 593. Mittelmeier, Jahr. Agrik. Chem. 1895, 199. Schiebler and Mittelmeier, Ber. 1893, **26**, 2930. V. Syniewski, Ann. 1899, **309**, 282; Chem. Centr. 1902, **73**, II, 984; Akad. Krakau, 1902, 28. M. Robinson, U. S. P. 163809, 1875. R. Brenner, U. S. P. 237366, 1881. C. Haynes, U. S. P. 320249, 1885. J. Beirmeister, U. S. P. 493905, 1893. W. Adamson, E. P. 381, 1875. J. Kelly, E. P. 17260, 1887; abst. J. S. C. I. 1889, **8**, 204. A. Cajot, E. P. 18732, 1890. L. Briant and W. Walker, E. P. 23748, 1892. T. Milligan, E. P. 12910, 1900; abst. J. S. C. I. 1900, **19**, 1027. C. Eckman, E. P. 8331, 1901. F. Planchon, E. P. 4956, 1908. C. Hervey, E. P. 20484, 1908. J. D'Orlowski, F. P. 405187, 1909; abst. J. S. C. I. 1910, **29**, 230. H. Alschech, F. P. 405711, 1909; abst. J. S. C. I. 1910, **29**, 440. H. Cambron, F. P. 447845, 1912; abst. J. S. C. I. 1913, **32**, 248. T. Calow & Co. D. R. P. 3854, 1878. Leinhass and Huelsenberg, D. R. P. 15531. Bellnas, D. R. P. 160975. M. Drucker, D. R. P. 16430, 1881. Klopfer, D. R. P. 187590. Kandler, Aust. P. 32974, 1907. See also D. R. P. 22716, addn. 24942, 1883. 26521, addn. 32256, 1884. 16373, addn. 36850, 1885. 34031, addn. 43943, 1887. 38397, addn. 39043, 1886. 45080, addn. 70505, 1891. 50442, addn. 57049, 1890. 52578, addn. 68620, 1892. 68074, addn. 70248, 1893. For production of starch in U. S. see T. Wagner, J. S. C. I. 1909, **28**, 343. W. Kaufmann, J. S. C. I. 1910, **29**, 527. C. Chandler, J. S. C. I. 1900, **19**, 617. Oil, Paint and Drug Rep. Aug. 7, 1911; abst. J. S. C. I. 1911, **30**, 1080. For the production of starch in Germany see Chem. Ztg. 1890, **14**, 305; abst. J. S. C. I. 1890, **9**, 526. Board of Trade J. 1900, 715; abst. J. S. C. I. 1901, **29**, 85. For the production of starch in Damascus, Turkey, see Foreign Office Annual Series No. 2832; abst. J. S. C. I. 1902, **21**, 1004. For production of starch in Egypt, see Board of Trade J. Oct. 10, 1901; abst. J. S. C. I. 1901, **20**, 1046.

[1] Mem. de l'Acad. 1690.

[2] "Usage des Feuilles," 1754.

[3] Phil. Trans. 1772.

[4] "Experiences sur l'action de la lumiere solaire," 1788.

[5] "Recherches chimiques sur la Vegetation," 1804.

[6] "Unters. ueber die Anatom. Verhältnisse des Chlorophylls," Botan. Zts. 1859, 225.

drew attention to the almost universal occurrence of starch grains in chlorophyl granules, and pointed out—in no hazy way—that starch grains were secondary formations within the corpuscles. These observations in general, were confirmed and extended by J. Schrader,[1] C. Kirchoff,[2] A. Payen,[3] J. Biot and J. Persoz,[4] G. Guerin-Vary and M. Chevreul,[5] Dubrunfaut,[6] Mayet,[7] V. Jacquelain,[8] A. Bechamp,[9] N. de Saussure,[10] F. Raspail,[11] O. Masche,[12] C. Jessen,[13] E. Lippmann,[14] W. Delffs,[15] H. Dragen-

---

1. Schweig. Jour. 1812, **4**, 108.

2. Schweig. Jour. 1815, **14**, 385, 389. See also, Schweig. Jour. **4**, 108.

3. Ann. Chim. Phys. 1834, **56**, 337; 1836, **61**, 355; Dingl. Poly. 1846, **102**, 323; Compt. rend. 1846, **22**, 687; 1861, **53**, 1217; 1865, **61**, 512. Ann. Chim. Phys. 1865, (4), **4**, 286; Bull. Soc. Chim. 1865, **3**, 470; Rep. Chim. appl. 1862, **4**, 36; J. Pharm. (4), **1**, 363; Vierteljahrschr. prakt. Pharm. **25**, 221; Dingl. Poly. 1862, **164**, 144; 1865, **178**, 69; Jahr. Chem. 1861, **14**, 717; 1865, **18**, 597; Chem. Centr. 1865, **36**, 845. A. Payen and J. Persoz, Ann. Chim. Phys. 1833, (2), **53**, 73; abst. J. Chim. med. 1833, **9**, 417; Pogg. Ann. Phys. 1834, **32**, 174; Berz. Jahr. Chem. 1835, **14**, 281.

4. Ann. Chim. Phys. 1833, (2), **52**, 72; Mus. His. Nat. Nouv. Ann. 1833, **2**, 109; Ann. 1833, **6**, 209; Acad. Sci. Mem. 1835, **13**, 437; Pogg. Ann. 1834, **32**, 160; Schweig. Jour. 1833, **68**, 163.

5. L'Institut, 1833, **1**, 101; Ann. Chim. Phys. 1834, **56**, (2), 225; J. prakt. Chem. 1834, **3**, 329; J. de Pharm. 1834, **20**, 690; Ann. 1835, **13**, 71; Ann. Chim. Phys. 1834, (2), **57**, 108. Ann. Chim. Phys. 1835, (2), **60**, 32; Ann. 1836, **17**, 261. L'Inst. 1835, **3**, 157; Ann. Chim. Phys. 1836 (2), **61**, 66; J. prakt. Chem. 1835, **5**, 19; 1836, **7**, 205; Compt. rend. 1836, **2**, 116. M. Chevreul, Mus. Hist. Nat. Nouv. Ann. 1834, **3**, 239; J. prakt. Chem. 1834, **2**, 382; Ann. 1835, **16**, 216.

6. Ann. Chim. Phys. 1847, (3), **21**, 178; Compt. rend. 1847, **25**, 308; 1849, **29**, 51; Pharm. Centr. 1848, **19**, 10; 1849, **20**, 643; Jahr. Chem. 1847–1848, **1**, 793; 1848, **2**, 464; J. prakt. Chem. 1847, **42**, 425; Annuaire de Chim. 1848, **4**, 260.

7. J. de Pharm. 1847, (3), **11**, 81; abst. Pharm. Centr. 1847, **18**, 393; Dingl. Poly. 1847, **104**, 107; Jahr. Chem. 1847–1848, **1**, 794. Elsner's Chem. Tech. Mitth. 1846–48, **1**, 116; Annuaire de Chim. 1848, **4**, 359.

8. Ann. Chim. Phys. 1840, (2), **73**, 167; 1843, (3), **8**, 255; Compt. rend. 1839, **7**, 916; L'Inst. 1843, 172; abst. Berz. Jahr. Chem. 1842, **21**, 326; 1845, **24**, 457; J. prakt. Chem. 1843, **30**, 477.

9. Compt. rend. 1854, **39**, 653; L'Inst. 1854, 338; J. prakt. Chem. 1855, **64**, 38; Pharm. Centr. 1854, **25**, 863; Jahr. Chem. 1854, **7**, 622. Compt. rend. 1856, **42**, 1210; Ann. Chim. Phys. 1856, (3), **48**, 458; L'Inst. 1856, 234; Ann. 1856, **100**, 364; Jahr. Chem. 1856, **9**, 670; J. prakt. Chem. 1856, **69**, 447. See also, L. Soubeiran, Jr., J. Pharm. (3), **25**, 89, 175; abst. Jahr. Chem. 1854, **7**, 621. J. J. Field, Pharm. J. Trans. **14**, 253; abst. Jahr. Chem. 1854, **7**, 621. O. Maschke, J. prakt. Chem. 1854, **61**, 1; abst. Pharm. Centr. 1854, **25**, 337; Jahr. Chem. 1854, **7**, 621.

10. Phil. Trans. 1819, 29; Ann. Chim. Phys. 1819, (2), **11**, 379; Gilb. Ann. 1820, **64**, 113; Giorn. Arcad. 1819, **4**, 227; J. de Pharm. 1819, **5**, 448; Schweig. J. 1819, **27**, 301; Trommsdorff, N. J. d. Pharm. 1820, **4**, St. 2, 112.

11. Ann. Sci. nat. 1825, **6**, 224, 384; 1826, **7**, 325; Quart. J. Sci. 1826, **21**, 176; 1827, **1**, 496; Soc. Philom. N. Bull. 1826, 155; Bull. Sci. Math. 1826, **6**, 333, 361; 1827, **8**, 200, 204, 264.

12. J. prakt. Chem. 1852, **56**, 400; 1854, **61**, 1; abst. Pharm. Centr.

dorff,[1] J. Wiesner,[2] A. Famintzin,[3] F. Flueckiger[4] and Fittig,[5] and especially by K. Naegeli[6] and Cramer.[7]

1852, **23**, 609; 1854, **25**, 337; J. de Pharm. 1854, **25**, 237; Jahr. Chem. 1852, **5**, 657; 1854, **7**, 621.

[13] Pogg. Ann. 1859, **106**, 497; 1860, **100**, 361; 1864, **122**, 482; Rep. Chim. Pure, 1859, **1**, 432; Vierteljahrschr. prakt. Pharm. **9**, 77; Chem. Centr. 1865, **36**, 128; Jahr. Chem. 1859, **12**, 544, 545; 1864, **17**, 571. J. prakt. Chem. 1868, **105**, 65; abst. Jahr. Chem. 1868, **21**, 763; Wag. Jahr. 1868, **14**, 458.

[14] J. prakt. Chem. 1861, **83**, 51; abst. Chem. News, 1862, **5**, 98; Chem. Centr. 1861, **32**, 859; Dingl. Poly. 1861, **162**, 450; Poly. Centr. 1862, **28**, 349; Wag. Jahr. 1861, **7**, 359.

[15] Jahr. Ver. Naturk. 1859–1860, **26**, 28; Pogg. Ann. 1860, **109**, 648; J. de Pharm. 1860, **38**, 336.

[1] Pharm. Zts. Russ. 1862, **1**, 41; Ill. Deut. Gewerbeztg. 1862, 283; Schweizer Zts. Pharm. **7**, 158; Rep. Chim. Appl. 1863, **5**, 186; Chem. News, 1863, **7**, 51; J. Landw. 1862, **7**, 206, 211; Wilda's Landw. Centr. 1862, 317; Chem. Centr. 1862, **33**, 523; Chem. Tech. Rep. 1862, **1**, II, 85; Dingl. Poly. 1864, **171**, 468; Jahr. Chem. 1862, **15**, 631; Wag. Jahr. 1862, **8**, 406; Zts. anal. Chem. 1862, **1**, 489.

[2] Dingl. Poly. 1868, **190**, 154; Jahr. Chem. 1868, **21**, 986; Wag. Jahr. 1868, **14**, 460; Poly. Centr. 1869, **35**, 284; D. Ind. Ztg. 1868, 464.

[3] A. Famintzin and J. Borodin, St. Petersb. Acad. Sci. Bull. 1868, **12**, 113; Ann. Sci. nat. 1867, **8**, 348; Bot. Ztg. 1867, **25**, 385. Heidelberger Jahrb. der Litteratur, 1869, 226.

[4] Pharm. Zts. Russ. 1868, **7**, 399. J. C. S. 1871, **24**, 543; Arch. Pharm. 1871, 145.

[5] Ueber die Konstitution der sogenannten "Kohlenhydrate," Tuebingen, 1871.

[6] Botan. Mitth. 1863, 387, 415; Sitzungsber. mathem-physik. Klasse der k. B. Akad. Wiss. München, 1881, 391; Botan. Ztg. 1881, **39**, 633. In Bied. Centr. 1882, 186; abst. J. C. S. 1882, **42**, 761, K. Naegli contributes a paper on the growth of starch grains by intussusception, in which he denies the correctness of the work of A. Schimper (Bied. Centr. 1881, 195, 479; Botan. Ztg. 1880, **38**, 881; 1881, **39**, 185; Ann. Sci. nat. (Bot.) 1880–1881, **11**, 256, 265; Quart. J. Micro. Sci. 1881, **21**, 291; abst. J. C. S. 1881, **40**, 1061. See also K. Naegeli, Flora, 1856, No. 38–41. Vierteljahrschr. prakt. Pharm. **6**, 256; Instit. 1863, 263; abst. Jahr. Chem. 1857, **10**, 493; 1859, **12**, 544; 1863, **16**, 571. L. Melsens, Acad. Sci. Bull. 1856, **23**, II, 663; Instit. 1857, 161; abst. Jahr. Chem. 1857, **10**, 493. Compare also, W. Naegeli, Ann. 1874, **173**, 218; abst. Chem. News, 1874, **30**, 229; J. C. S. 1875, **28**, 55; Poly. Centr. 1874, **40**, 1297; Chem. Centr. 1874, **45**, 809; Jahr. Chem. 1874, **27**, 878; Jahr. rein chem. 1874, **2**, 176; Wag. Jahr. 1874, **20**, 653. J. Boehm Sitzber. k. Akad. Wien, 1856, **22**, 179; Sitzber. k. Akad. der Wiss. 1874, **69**, 76; 1876, **73**. Wiener Anzeiger, 1874, **11**, 47; 1876, **13**, 12; Landw. Versuchstat. 1879, **23**, 123; abst. Chem. News, 1877, **36**, 242; J. C. S. 1876, **29**, 952, 953. Ber. 1876, **9**, 123; 1877, **10**, 1804; abst. J. C. S. 1878, **34**, 84; 1879, **36**, 551; Chem. Centr. 1875, **46**, 202, 207, 217, 233, 248; 1876, **47**, 109, 473, 488; 1878, **49**, 53, 684; Jahr. Chem. 1876, **29**, 861; 1877, **30**, 924; 1878, **31**, 944; Jahr. rein chem. 1876, **4**, 375. Botan. Ztg. 1883, **41**, 33, 49; abst. Jahr. Chem. 1883, **36**, 1390; J. C. S. 1883, **44**, 820; Chem. Centr. 1883, **54**, 317. He employed for the first time the now well-known method of detecting minute starch granules by successive treatment with caustic potash and iodine.

[7] "Pflanzenphysiologische Untersuchungen," 1858. According to P. Kögel (Biochem. Zts. 1919, **95**, 313; abst. J. C. S. 1919, **116**, i, 471; J. S. C. I. 1919, **38**, 738-A) keto-enol changes probably play an important rôle in the photosynthesis of formaldehyde and sugar. See A. Schimper, Bied. Centr. 1881, 479; J. C. S. 1881, 1061; Botan. Zts. 1880, 881; 1883, Nos. 7–10; 1885, 738.

It was in 1862 when J. Sachs[1] showed that starch grains do not occur in etiolated chlorophyl granules, and that their formation in normal corpuscles is dependent upon exposure to light.[2] Although adducing no experimental data to back him up, he assumed that starch grain formation only takes place when the assimilating organs are supplied with carbon dioxide. Godlewski substantiated his assumption.

It was next determined[3] that the volume of oxygen exhaled by assimilating organs is approximately equal to the carbon dioxide absorbed, a proportion which favors the assumption that a carbohydrate has been formed, as according to the equation:

$$6CO_2 + 5H_2O = C_6H_{10}O_5 + 6O_2$$

The work of N. Pringsheim,[4] J. Wiesner,[5] C. Kraus,[6] L.

---

[1] Botan. Ztg. 1862, **20,** 365; 1864, 289. Botan. Centr. 1884, **19,** 35; Arbeit Botan. Inst. Wuerzburg, 1884, **3,** 1. Chem. Centr. 1884, **55,** 945; J. C. S. 1885, **48,** 831; Ann. Landw. 1862, **39,** 181, 406; Jahr. Chem. 1884, **37,** 1433. He apparently was the first to suspect there is a distinct relation between the starch granules and the processes of assimilation. He established the fact that the appearance of starch in the chlorophyl granule is induced by, and is dependent upon, the action of light of sufficient intensity, and that the green coloring matter of the chloroplast is essential to the production of this autochthonous starch as it is for the decomposition of carbon dioxide, for the decolorized chloroplasts of an etiolated plant have not this power, so long as they remain colorless, to produce starch within their substance. Sachs for the first time clearly formulated the proposition that the production of starch in the chlorophyl granule is directly connected with assimilation, and that when plants are confined in the dark the starch disappears from their chloroplasts, to again reappear when the plants are once more illuminated. This is indicative of a daily periodic change in green leaves, the starch which is formed in the chloroplast in the daylight hours being wholly or partially redissolved and removed from the leaf during the night, to supply the constant demands of the growing parts of the plant.

[2] Flora, 1873, 378; Arbeiten d. bot. Instit. Wuerzburg, 1874, **1,** 343. W. Pfeffer (Monatsh. d. Berliner Akad. 1873, 784. Botan. Ztg. 1871, **29,** 319; 1872, **30,** 425, 449, 465. Belgique Horticole, 1872, **22,** 248; 1873, **23,** 119; J. C. S. 1872, **25,** 1107; Ann. Phys. Chem. 1783, **148,** 86; Chem. News, 1873, **27,** 133; Jahr. Chem. 1871, **24,** 186; 1873, **26,** 167) proved that when plants are placed in air entirely free from CO_2, no starch was formed in the chloroplasts even when the plants were exposed to intense light for prolonged periods. Godlewski found that previously formed starch completely disappeared from the chloroplasts under these conditions, and on the other hand, that starch formation within these bodies could be materially accelerated by increasing, within certain limits, the amount of carbon dixoide in the air around the plant. These results materially strengthened the earlier conclusions of Sachs that autochthonous starch formation and assimilation go hand in hand.

[3] J. Boussingault, Compt. rend. 1861, **53,** 862; Ann. Sci. nat. (Bot.), 1862, **16,** 5; Pharm. J. Trans. (2), **3,** 479; Ann. Chim. Phys. 1862, (3), **66,** 295; Mon. Sci. 1861, **3,** 621; Rep. Chim. appl. 1861, **3,** 449; Jahr. Chem. 1861, **14,** 733.

[4] Monatsh. d. Berl. Akad. 1874, 628; 1875, 745; 1879, 532. J. Bot. 1875, **4,** 114; Bot. Soc. Trans. 1876, **12,** 258; Bot. Ztg. 1879, **37,** 789, 811;

Pfaundler,[1] F. Kromayer[2] and C. Timiriazeff[3] shed but little additional light. However, it has long been known that starch granules only grow and increase in size when they are in contact with protoplasm and are exposed to sunlight at a favorable temperature and in the presence of sufficient carbon dioxide. The formation of starch in plants, therefore, must be regarded primarily as a product of assimilation, and may be assumed, in addition to the carbohydrate reaction expressed above, to be possible of occurrence in somewhat like the following manner. A. Bayer,[4] reasoning from the point that carbohydrates may be oxidized to aldehydes, propounded that formaldehyde is the immediate product of assimilation, and by its condensation, polymerizes six times to glucose, and from this to its anhydride, which is starch. As S. Vines[5] has pointed out, if this be so, then the primary function of chlorophyl in plants is merely the decomposition of carbon dioxide to carbon monoxide and oxygen.

T. Bokorny[6] rather corroborates the above, and using Spirogyra as the material for the investigation, concluded that starch is formed from methylal. He was unable to observe any formation of starch in the absence of light, but when the Spirogyra was immersed in dilute methylal in sunlight abundant starch formation took place. According to Bokorny, glycol and glycerol can

Ann. Mag. Nat. Hist. 1880, **5**, 62; Jahr. Botan. 1879–1881, **12**, 288; 1882, **13**, 377. See also Conrad, Flora. 1872.

5. Entstehung des Chlorophyls, Wien, 1877.

6. Flora, 1875, **58**, 155, 206, 232, 253, 268, 346, 365, 381, 489.

[1] Ann. 1860, **115**, 37; abst. Chem. News, 1860, **2**, 310; Rep. Chim. Pure, 1861, **3**, 28; Chem. Centr. 1860, **31**, 851; Jahr. Chem. 1860, **13**, 531.

[2] Arch. Pharm. 1861, **156**, 164; Chem. Centr. 1861, **32**, 393; Jahr. Chem. 1861, **14**, 738.

[3] Compt. rend. 1877, **84**, 1236; 1890, **110**, 1346. Ann. Sci. nat. (Bot.) 1885, **2**, No. 2; Chem. News, 1886, **53**, 180. J. C. S. 1874, **27**, 285; 1877, **32**, 635; 1885, **48**, 714; 1886, **50**, 626. Ann. Chim. Phys. 1877, (5), **12**, 355. Ber. 1873, **6**, 1212; 1885, **18**, R, 286; 1886, **19**, R, 355; Jahr. Chem. 1873, **26**, 168; 1877, **30**, 196; 1883, **36**, 1397; 1885, **38**, 1797.

[4] Ber. 1870, **3**, 63; abst. J. C. S. 1871, **24**, 331; Jahr. Chem. 1870, **23**, 897.

[5] J. C. S. 1878, **33**, 376; Chem. News, 1878, **37**, 190; abst. Ber. 1878, **11**, 1263; Jahr. Chem. 1878, **31**, 939.

[6] Ber. botan. Ges. 1888, **6**, 116; 1891, **9**, 103; Landw. Versuch-Stat. 1889, **36**, 229; abst. Chem. News, 1891, **64**, 17; J. C. S. 1889, **56**, 67; 1891, **60**, 1539; J. S. C. I. 1893, **12**, 281; Ber. 1892, **25**, R, 471; Chem. Centr. 1888, **59**, 858; 1891, **62**, 120; Chem. Ztg. Rep. 1889, **13**, 312; 1891, **15**, 167; Jahr. Chem. 1889, **42**, 2084; 1891, **44**, 2179, 2206. Chem. Ztg. 1896, **20**, 1005; abst. J. C. S. 1898, **74**, ii, 41; J. S. C. I. 1897, **16**, 154; Chem. Centr. 1897, **68**, I, 177; Jahr. Chem. 1896, **49**, 1020.

also form starch.[1,2] The methylal in the presence of sodium hydroxymethyl sulfonate and dipotassium phosphate, when allowed to remain in carbon dioxide-free air but exposed to light, after five days showed considerable quantities of starch, the sodium hydroxymethyl sulfonate being split up into sodium sulfite and formaldehyde, and this in turn, condensed and became converted into starch.

J. Boehm, in his work on the formation of starch in chlorophyl granules,[3] pointed out that light of any intensity sufficient to enable green plants to decompose carbon dioxide, effects also the transfer of starch from the leaves to the chlorophyl granules, and that in direct sunshine, transfer of recognizable amounts of starch in chlorophyl granules from the stems to the leaves, takes place in 10–15 minutes. It is obvious that experiments on the formation of starch in chlorophyl granules consequent on direct assimilation of carbon dioxide can only be made with plants perfectly free from starch, or with detached leaves free from starch. From his experiments on plants of *Phoscalus multiflorus*, the conclusion is drawn[4] that the statement that the starch of chlorophyl grains is in all cases a product of the intrinsic synthesis from CO_2 and water, is fallacious. His work leads to the following two conclusions: (1) the formation of starch in chlorophyl grains is in many cases the result of a metamorphosis of bodies not intrinsic to the cells in which this conversion takes place, but liberated elsewhere by the plant; and, (2) that the process of conversion is entirely independent of the action of light. In this connection,

---

[1] Compare, K. Miyake, Bot. Mag. Tokyo, 1900, **14**, 158; Botan. Centr. 1901, **85**, 389; Bied. Centr. 1902, **31**, 753; J. C. S. 1903, **84**, ii, 96. E. Mer, Compt. rend. 1891, **112**, 248, 964; abst. J. C. S. 1891, **60**, 604; Chem. Centr. 1891, **62**, I, 509; Chem. Ztg. Rep. 1891, **15**, 154.

[2] A. Mayer, Botan. Ztg. 1886, 697, 713; abst. J. C. S. 1887, **52**, 460; Chem. Centr. 1887, **58**, 6.

[3] Sitzber. k. Akad. Wien, 1856, **22**, 179; Sitzber. k. Akad. der Wiss. 1874, **69**, 76; 1876, **73**. Wiener Anzieger, 1874, **11**, 47; 1876, **13**, 12. Landw. Versuchstat. 1879, **23**, 123; abst. Chem. News, 1877, **36**, 242; J. C. S. 1876, **29**, 952, 953; Ber. 1876, **9**, 123; 1877, **10**, 1804; abst. J. C. S. 1878, **34**, 84; 1879, **36**, 551; Chem. Centr. 1875, **46**, 202–207, 217, 233, 248; 1876, **47**, 109, 473, 488; 1878, **49**, 53, 684; Jahr. Chem. 1876, **29**, 861; 1877, **30**, 924; 1878, **31**, 944; Jahr. rein chem. 1876, **4**, 374. Botan. Ztg. 1883, **41**, 33, 49; abst. Jahr. Chem. 1883, **36**, 1390; J. C. S. 1883, **44**, 820; Chem. Centr. 1883, **54**, 317.

[4] Ber. 1877, **10**, 1804; abst. J. C. S. 1878, **34**, 84. Bied. Centr. 1883, 212; 1884, 316; abst. J. C. S. 1883, **44**, 820; 1884, **46**, 1250. Zts. gesammte Brauwesen, 1883, 76.

reference is directed to the work of L. Schulze,[1] R. Sachsse,[2] E. Ebermayer,[3] O. Boettger,[4] J. Baranetzky[5] and Bouillon-Lagrange and Vauquelin.[6]

G. Belluci[7] tried the effect of the presence of various substances in order to determine whether the production of starch under the influence of sunlight and subsequent reconversion at night, is to be properly regarded as a physiological or a chemical change. It was found that chloroform and ether vapor destroy chlorophyl and prevent the transformation of starch during sunlight, and that the function of chlorophyl was also diminished by the presence of CO_2. Saccharification of starch proceeds in the dark. From the above, it would appear that the phenomena is a physiological change.[8] The presence of organic acids as

---

[1] J. prakt. Chem. 1883, **136**, 311; abst. Chem. News, 1884, **49**, 70; J. C. S. 1884, **46**, 284; Bull. Soc. Chim. 1884, **42**, 292; Ber. 1883, **16**, 1364; Chem. Tech. Rep. 1883, **22**, II, 133; Chem. Ztg. 1883, **7**, 1552; Jahr. Chem. 1883, **36**, 1366; Wag. Jahr. 1883, **29**, 671; Zts. deut. Spiritusfabr. 1883, 1022.

[2] Leipziger Naturf. Ges. Ber. 1877, 30; abst. Chem. News, 1879, **39**, 264; Chem. Centr. 1877, **48**, 732; Chem. Tech. Rep. 1878, **17**, I, 297; Jahr. Chem. 1877, **30**, 898; Jahr. rein chem. 1877, **5**, 175; Zts. Chem. Grossgew. 1877, **2**, 588.

[3] "Physiologische der Pflanzen," Berlin, 1882, **1**, 194.

[4] Dingl. Poly. 1873, **210**, 79; abst. Jahr. Chem. 1873, **26**, 962.

[5] "Die Staerke umbildenden Fermente in den Pflanzen," Leipzig, 1878.

[6] Bull. Pharm. **3**, 54, 395. A. Schimper, Bot. Ztg. 1880, 881; 1881, 186; Ann. Sci. nat. (Bot.) 1880–1881, **11**, 256, 265; Quart. J. Micro, Sci. 1881, **21**, 291; J. C. S. 1881, **40**, 1061; Bied. Centr. 1881, 195, 479. His work upon the development of the starch granule in plants was classical. He carried our knowledge a step further by indicating how closely the shape of the starch granule is dependent upon the shape of the chlorophyl body which gives rise to it, and upon the position it occupies with regard to the chlorophyl-body during its development. He demonstrated that in all parts of the plant in which starch is being deposited, either as reserve- or transitory-starch, the starch granules in process of development are not surrounded immediately by ordinary protoplasm, but are contained in, or attached to, peculiar spherical or spindle-shaped refrangible corpuscles. These are the starch-forming corpuscles or amyloplasts, which are casually related to the deposition of the starch granules in the non-chlorophyllous parts of the plant, just as are the chlorophyl bodies on the other hand, in the green assimilating cells. As indicating the close analogy existing between the amyloplasts and the chloroplasts as regards structure, development and starch-producing function, it was observed that amyloplasts may, under favorable conditions of light, actually be converted into chlorophyl corpuscles capable of assimilating in the usual manner, and that, in fact, this conversion goes on normally and regularly in the development of the plant organ.

[7] Ann. chim. farm. 1887, (4), **5**, 217; Staz. sperim. agrar. **14**, 77; Gazz. chim. ital. 1888, **18**, 77; abst. J. C. S. 1887, **52**, 1136; Chem. Centr. 1887, **58**, 572; 1888, **59**, 671, 977; Jahr. Chem. 1887, **40**, 2285; 1888, **41**, 2348.

[8] See G. Bonnier and L. Mangin, "Recherches sur l'action chlorophyllienne," Ann. Sci. nat. (Bot.) 1886, **3** (7), 5; Compt. rend. 1884, **99**,

citric,[1] renders the action of diastase on starch in the plant more rapid. G. Carboni[2] estimates the amount of starch formed by blanching the leaves with KOH and absolute alcohol, then immersing in a saturated solution of iodine, and judging by the depth of color produced.[3,4,5,6,7]

E. Laurent[8] plunged etiolated shoots of potato plants in which the reserve material was exhausted, and in which no trace of starch could be found, into solutions of different organic compounds in the dark. Starch was formed from only glycerol, dextrose, levulose, galactose, saccharose, lactose and maltose.[9,10] It would appear[11,12,13] that salt has a distinct influence (inhibitory in large

160; 1885, **100**, 1092, 1303; 1886, **102**, 123; France Soc. Bot. Bull. 1885, **32**, 204, 368; abst. J. C. S. 1886, **50**, 387; Ber. 1885, **18**, R, 387; 1886, **19**, 107; Jahr. Chem. 1884, **37**, 1431; 1885, **38**, 1787, 1796; 1886, **39**, 1807.

1. W. Detmer, Jenaische Sitzber. 1881, 22; Bot. Ztg. 1883, **41**, 601; abst. Bied. Centr. 1882, **11**, 110; J. C. S. 1882, **42**, 640. Zts. physiol. Chem. **7**, 1; abst. Bied. Centr. 1883, **12**, 71; 1884, **13**, 69; Chem. News, 1884, **50**, 35; J. C. S. 1882, **42**, 881; 1883, **44**, 631; 1884, **46**, 917, 1063, 1402; Ber. 1882, **15**, 2924; Chem. Centr. 1882, **53**, 46; Jahr. Chem. 1882, **35**, 1233. See also P. Deherain and L. Maquenne, Ann. Agronom. **7**, 385; **12**, 526; Compt. rend. 1885, **100**, 1234; **101**, 887, 1020; 1886, **103**, 167; abst. Chem. News, 1885, **52**, 47; 1886, **54**, 237; J. C. S. 1882, **42**, 639; 1885, **48**, 927; 1886, **50**, 170, 273, 1062; 1887, **52**, 172; Ber. 1885, **18**, R, 387, 711; Jahr. Chem. 1885, **38**, 1788; 1886, **39**, 1801.

2. Revista de Vitisoltura ed Enologia Italiana, **9**, 13; Ann. Agronom. **11**, 85, 236; J. C. S. 1885, **47**, 683, 1004.

3. O. Kellner, Landw. Jahr. 1879, 243; Bied. Centr. 1879, **8**, 671; abst. J. C. S. 1880, **38**, 279, 731; Chem. Centr. 1879, **50**, 744, 761; Jahr. Chem. 1879, **32**, 887. Versuchstat. 1885, **32**, 57. O. Kellner, Y. Mori and M. Nagaoka, Zts. physiol. Chem. 1890, **14**, 297; abst. J. C. S. 1890, **58**, 281; Ber. 1891, **24**, R, 532; Chem. Centr. 1890, **61**, I, 909; Jahr. Chem. 1889, **42**, 2285; Wag. Jahr. 1890, **36**, 1011; Zts. ang. Chem. 1890, **3**, 408.

4. O. Eberdt, "Origin and Development of Starch Grains," Pringsheim's Jahr. 1891, **22**, 293.

5. K. Goebl, "Beitraege zur Morphologie u. Physiologie des Blattes," Bot. Ztg. 1882, Nos. 22–25.

6. Callot, Crell's Chem. J. **5**, 140.

7. E. Bruecke, Wien. Akad. Ber. 1873, (3), **65**, 126; J. C. S. 1873, **26**, 394, 395; Bull. Soc. Chim. 1873, **20**, 86.

8. "Recherches experimentales sur la formation d'amidon dans les plantes," Brussels, 1888. Botan. Ztg. 1886, 151. Ann. Agronom. **14**, 273; abst. J. C. S. 1888, **54**, 1126.

9. Hebert, Bull. Assoc. Chim. 1897, **14**, 1003; abst. J. S. C. I. 1897, **16**, 623. Ann. Agron. **17**, 97; abst. J. C. S. 1891, **60**, 1285.

10. R. Kayser, "Ueber Vorkommen von Rohrzucker und einigen seiner Umwandlungsproducte im Organismus des Pflanzen." Landw. Versuchs-Stat. 1883, **29**, 461.

11. P. Lesage, Compt. rend. 1891, **112**, 672; abst. J. C. S. 1891, **60**, 856; Ber. 1891, **24**, R, 372; Chem. Centr. 1891, **62**, I, 833; Jahr. Chem. 1891, **44**, 2206.

12. P. Lesage, Compt. rend. 1891, **112**, 891; abst. J. C. S. 1891, **60**, 1133; Chem. Centr. 1891, **62**, I, 1063.

13. P. Lesage, Compt. rend. 1891, **113**, 373; abst. J. C. S. 1892, **62**, 92.

amounts) on general starch formation in chlorophyllian organs.[1]

Carbohydrates migrate out of leaves much more quickly when on the plant, than when cut off and laid in water. Whereas in spring and summer all starch disappears in 1–2 days, in winter the process requires 7–14 days. W. Saposchnikoff[2] was able to determine the rate of formation of carbohydrates in leaves by first determining the amount originally present, and the rate of migration allowed for. Then the amount of carbohydrates formed (in grams) per square meter of leaf surface per hour, was determined for a series of days of varying climatic changes.[3] According to A. Meyer[4] and E. Acton,[5] the percentage of starch formation in a given period is augmented by the addition of glucose, cane sugar, glycerol and inulin. The splitting off of water is said to be necessary.

J. Grüss,[6] in determining the time required under varying conditions of germination for starch granules to spread in the bud-sheath and appear in the calyptra (which in the quiescent stage is free from starch), found that oxygen was necessary for starch formation, which only begins at a few degrees above 0°. At low temperatures the growth of the granules appears very limited.[7,8]

---

1. H. Pick, Ann. Agron. **10,** 274; Botan. Centr. **16,** 281, 314, 343, 375; J. C. S. 1884, **46,** 1402.
2. Ber. bot. Ges. 1889, **7,** 258; 1890, **8,** 233; 1891, **9,** 293; Just's Bot. Jahr. 1889, **1,** 25; J. C. S. 1891, **60,** 762; Chem. Centr. 1889, **60,** II, 371; 1891, **62,** I, 93; 1892, **63,** I, 320; Dingl. Poly. 1890, **275,** 428; Jahr. Chem. 1889, **42,** 2083; 1890, **43,** 2794; 1891, **44,** 2205; 1892, **45,** 2156.
3. J. Reinke, Ber. bot. Ges. 1881, 2144; Just's Bot. Jahr. 1881, **1,** 141, 395; Ber. 1881, **14,** 2144; Pharm. J. Trans. (3), **15,** 268; abst. J. C. S. 1882, **42,** 243; 1885, **48,** 182; Bull. Soc. Chim. 1887, **37,** 378; Chem. Centr. 1884, **55,** 220; Jahr. Chem. 1881, **34,** 1006; 1884, **37,** 1429, 1438. See also O. Löw and T. Bokorny, Ber. 1881, **14,** 2508; abst. Jahr. Chem. 1881, **34,** 1006.
4. Bot. Ztg. 1881, 841; 1886, 81, 697, 713. Ber. bot. Ges. 1891, **9,** 238; Pringsheim's Jahr. 1890, **21,** 520; Bied. Centr. 1882, **11,** 396; J. C. S. 1882, **42,** 1122; 1886, **50,** 902. Ann. Agron. **12,** 209.
5. Proc. Roy. Soc. 1890, **47,** 150; abst. J. C. S. 1890, **58,** 818, 1021; J. S. C. I. 1890, **9,** 634; Chem. Centr. 1890, **61,** I, 168; Jahr. Chem. 1889, **42,** 2084; 1890, **43,** 2170; Naturw. Rundsch. **4,** 594. Cf. A. Meyer, Bot. Ztg. 1886, 81, 105, 129, 145; abst. Ann. Agron. **12,** 209; J. C. S. 1886, **50,** 902.
6. Wochen. f. Brauerei, 1897, **14,** 321, 409, 487; abst. J. S. C. I. 1897, **16,** 691; Chem. Centr. 1897, **68,** II, 363, 665, 903; Wag. Jahr. 1897, **44,** 917; see also F. Reinitzer, Wochen. f. Brauerei, 1897, **14,** 486; abst. Chem. Centr. 1897, **68,** II, 903.
7. Wochen. f. Brauerei, 1898, **15,** 81, 269; 1899, **16,** 519; abst. J. S. C. I. 1898, **17,** 479; 1899, **18,** 1042; Mon. Sci. 1900, **55,** 527, 532; Chem. Centr. 1898, **69,** I, 785; II, 42; Jahr. Chem. 1898, **51,** 1332, 2688.
8. A. Marcacci, Staz. sper. agr. ital. **18,** 618; abst. J. C. S. 1891, **60,** 357; Bied. Centr. 1890, **19,** 792. Atti. Soc. Toscana Sci. Nat. 1890, **7,** 28; Jahr. Chem. 1890, **43,** 2152.

H. Brown and G. Morris,[1] in repeating the experiments of J. Boehm[2] and A. Meyer,[3] found that the chlorophyl granules form starch both by assimilation and by a process of elaboration from certain nutritive solutions of sugars. Inasmuch as the usual phyto-histological function of starch is as a reserve nutritive material (corresponding to fat in the animal organism), when needed it is rendered dialyzable by means of an enzyme such as diastase, and thereby converted into readily diffusable sugars.[4,5,6] There is no doubt but what under favorable climatic conditions, the plant is favored with the elaboration of more assimilable material than is necessary to enable it to perform its normal functions, and the accumulation of excess is manifested by the deposition of this water-insoluble compound, as a quickly liquidatable asset in time of need. Starch, therefore, is only called upon

---

[1] H. Brown and T. Glendinning, J. C. S. 1902, **81**, 388; Chem. News, 1902, **85**, 129; abst. J. S. C. I. 1902, **21**, 419; Chem. Centr. 1902, **73**, I, 775, 1065; Jahr. Chem. 1902, **55**, 231.

H. Brown and J. Heron, J. C. S. 1879, **35**, 596; Chem. News, 1879, **39**, 284; 1880, **41**, 22; Ann. 1879, **199**, 165; abst. Ber. 1879, **12**, 1477; Jahr. Chem. 1879, **32**, 838; Jahr. rein Chem. 1897, **7**, 507.

H. Brown and J. Millar, J. C. S. 1899, **75**, 315; Chem. News, 1899, **79**, 79, 80; abst. J. S. C. I. 1899, **18**, 159; Bull. Soc. Chim. 1899, **22**, 795, 797, 798; Chem. Centr. 1899, **70**, I, 674, 1108; Jahr. Chem. 1899, **52**, 1276, 1279. Trans. Guiness Research Lab. 1903, **1**, 79; abst. J. S. C. I. 1904, **23**, 137.

H. Brown and G. Morris, J. C. S. 1885, **47**, 527; 1889, **55**, 449; 1890, **57**, 458, 489; 1895, **67**, 309; Chem. News, 1885, **51**, 308; 1886, **53**, 37; 1889, **59**, 295; 1890, **61**, 201; 1895, **71**, 123; abst. Bull. Soc. Chim. 1890, **4**, 682; 1891, **5**, 543; 1896, **16**, 1006; J. S. C. I. 1885, **4**, 682; 1889, **8**, 716; 1895, **14**, 288; Ann. 1885, **231**, 72, 109, 125; Ber. 1885, **18**, R, 615; 1889, **22**, R, 740; 1890, **23**, R, 502; 1895, **28**, R, 642; Chem. Centr. 1889, **60**, II, 124, 285; 1890, **61**, I, 1006; II, 149; 1895, **66**, I, 849; Jahr. Chem. 1885, **38**, 1757; 1889, **42**, 136, 2063; 1890, **43**, 2174; 1895, **48**, 1335.

H. Brown, G. Morris and J. Millar, J. C. S. 1897, **71**, 109; Chem. News, 1897, **75**, 42, 43; abst. J. S. C. I. 1897, **16**, 166; Bull. Soc. Chim. 1897, **18**, 936, 937; Chem. Centr. 1897, **68**, I, 366, 367, 584, 585; Jahr. Chem. 1897, **50**, 1523, 1526.

H. Brown and S. Pickering, J. C. S. 1897, **71**, 783; Chem. News, 1897, **75**, 295, 296; abst. J. S. C. I. 1897, **16**, 624; Bull. Soc. Chim. 1897, **18**, 1062, 1190; 1898, **20**, 450; Chem. Centr. 1897, **68**, II, 169, 464; Jahr. Chem. 1897, **50**, 225, 1459.

[2] Sitzber. d. k. Akad. Wien, 1856, **22**, 479; 1876, 73. Ber. 1877, **10**, 1804. Bot. Ztg. 1883, 33, 49. Zts. gesammte Brauw. 1883, 76.

[3] Bot. Ztg. 1881, Nos. 51, 52; 1885, Nos. 27–32; 1886, 105, 129, 145, 697, 713; Ann. Agron. **12**, 209; abst. J. C. S. 1886, **50**, 902; 1887, **52**, 460; Chem. Centr. 1887, **58**, 6.

[4] O. Kohlrausch, Zts. Ver. Rübenzuckerind. 1885, **35**, 344; abst. Bied. Centr. 1885, **14**, 349; J. C. S. 1885, **48**, 1021; Wag. Jahr. 1885, **31**, 763.

[5] J. Habermann, Ann. 1874, **172**, 11; abst. J. C. S. 1874, **27**, 1077; Chem. Centr. 1874, **45**, 374; Jahr. Chem. 1874, **27**, 879.

[6] A. Dastre, Compt. rend. Soc. Biol. 1894, **46**, 375. A. Dastre and N. Floresco, Compt. rend. Soc. Biol. 1895, **47**, 669.

when assimilation ceases. These authors are of the opinion that cane sugar is probably the first polysaccharide to be synthesized, and may be regarded as the initial material for all the metabolic changes which occur in the plant. As a temporary reserve material, it accumulates in the sap at a time when the processes of assimilation are at their maxima. When the degree of concentration reaches a certain limit, then the chloroplasts commence to elaborate starch.[1,2,3,4]

As the result of a study of the action of light on chlorophyl, H. Wagner[5] suggests that the formation of starch, sugars and other carbohydrates in the green leaf may be initiated by the photo-oxidation of chlorophyl and subsequent elaboration of the aldehyde produced by the condensation (of oxidized chlorophyl) rather than by the direct photo-synthesis of carbon dioxide and water.[6]

As the conclusion to an elaborate investigation of the colloidal properties of starch in relation to its constitution,[7] E. Fouard has modified some of the views of H. Brown and G. Morris[8] on the functions of starch in relation to the living plant. As the result of an examination of the mineral constituents of starch,[9] disclosing the existence of acid and basic phosphates primarily, and by virtue of the action of acid and basic salts upon the coagulation of starch solution as pointed out by A.

---

[1] R. Chodat, "Transformation of Chlorophyll-grains into Amyliferous Leucites," Arch. Sci. Phys. nat. 1889, **22**, 602; 1890, **23**, 559; Geneve Soc. Phys. Mem. 1890–1893, No. 62, 63.

[2] A. Wigand, "Das Protoplasma als Ferment-organismus," Marburg, 1888.

[3] A. Wohl, Ber. 1890, **23**, 2084; abst. J. C. S. 1890, **58**, 1085; J. S. C. I. 1890, **9**, 957; Chem. Centr. 1890, **61**, II, 338; Chem. Tech Rep. 1890, **29**, II, 99; Jahr. Chem. 1890, **43**, 2143; Wag. Jahr. 1890, **36**, 825.

[4] E. Belzung, "Formation of Starch-grains and Chlorophyll-bodies," Ann. Sci. nat. (Bot.) 1891, **13**, 5. Cf. also Bull. France Soc. Bot. 1885, **32**, 374; 1886, **33**, 199, 483. Ann. Sci nat. (Bot.) 1887, **5**, 179; Rev. Sci. 1887, **40**, 788. J. Bot. 1887, **1**, 86, 97; 1891, **5**, 5; 1895, **9**, 33, 41, 61, 101, 134, 137, 181.

[5] Proc. Roy. Soc. 1914, **87**, B, 386; abst. C. A. 1914, **8**, 3451; J. C. S. 1914, **106**, i, 561. See also G. Ciamician and P. Silber, Ber. 1911, **44**, 1280.

[6] J. Cuboni, "Researches sue la formation de l'amidon dans les feuilles de la vigne," Archives Italiennes de Biologie, 1886, **7**, 209.

[7] Compt. rend. 1906, **142**, 796, 1163; 1907, **144**, 501, 1368; 1908, **146**, 285, 930, 980; **147**, 813, 931; 1909, **148**, 502, 978; abst. J. S. C. I. 1909, **28**, 433. Bull. Soc. Chim. 1909, **5**, 828; abst. J. S. C. I. 1909, **28**, 898.

[8] Loc. cit.

[9] See H. Brown and S. Pickering, loc. cit.

Fernbach,[1] and A. Fernbach and J. Wolff,[2] and also of the fact that the vegetable cell contains juices of variable reaction, it would appear plausible that the phosphatic content of the starch plays an important part in the migration of starch in the vegetable organism.[3,4,5,6]

A. Ursprung[7] has investigated the formation of starch in the leaves of *Phaseolus multiflorus*, etc., at different positions of the spectra of the sun and moon under the rays of different electric lights, and finds that the extreme limits of wave-length within which starch is formed are 760μ and 330μ. Synthetical processes of the types occurring in plants, may also in some cases be effected by the aid of the quartz-mercury lamp.[8] The following reactions have been studied from this point of view, and carried out through ultra-violet light:

$$CO + O \rightleftarrows CO_2 : CO + H_2 \rightleftarrows H.CHO : \chi CH_2O \rightleftarrows (CH_2O)\chi : H_2 + O \rightleftarrows H_2O.$$

Formamide has been obtained by exposing a mixture of CO and NH_3 to ultra-violet light.[9,10,11,12]

1. Ann. Brass. et Dist. 1908, **11**, 481. Chem. Ztg. 1908, **32**, 1068; abst. J. S. C. I. 1908, **27**, 1169.
2. Compt. rend. 1906, **143**, 363, 380; 1907, **145**, 80, 261; abst. J. S. C. I. 1906, **25**, 898; Rep. Chim. 1908, **8**, 61, 89.
3. C. Wehmer, "Zur Kohlenhydrat-Natur der Formose," Ber. 1887, **20**, 2614; abst. J. C. S. 1888, **54**, 40; Bull. Soc. Chim. 1888, **49**, 712; Jahr. Chem. 1887, **40**, 2248.
4. W. Spring, Bull. Cong. Chim. Pharm. Liege, 1905, **1**, 229. Bull. Soc. Belg. 1910, **24**, 112.
5. L. Roos and E. Thomas, Compt. rend. 1892, **114**, 593; abst. Chem. News, 1892, **65**, 167; J. C. S. 1892, **62**, 908; J. S. C. I. 1892, **11**, 627; Ber. 1892, **25**, R, 387; Jahr. Chem. 1892, **45**, 2156.
6. W. Hardy, Zts. physik. Chem. 1900, **33**, 326; abst. J. C. S. 1900, **78**, ii, 396; Chem. Centr. 1900, **71**, I, 898, 1196; Jahr. Chem. 1900, **53**, 35, 36.
7. Ber. bot. Ges. 1917, **35**, 69; abst. J. C. S. 1917, **112**, i, 504; C. A. 1917, **11**, 3301.
8. D. Berthelot and H. Gaudechon, Compt. rend. 1910, **150**, 1690; **151**, 316; abst. J. C. S. 1910, **98**, i, 543; C. A. 1910, **4**, 2408; J. S. C. I. 1910, **29**, 904; Chem. Zentr. 1910, **81**, II, 558, 876, 1038; Jahr. Chem. 1910, **63**, I, 639; II, 362, 380. J. Pharm. et Chim. 1910, (7), **2**, 5. Compt. rend. 1913, **156**, 68; abst. C. A. 1913, **7**, 1484; J. C. S. 1913, **104**, ii, 90; J. S. C. I. 1913, **32**, 160; Chem. Zentr. 1913, **84**, I, 694.
9. H. Le Chatelier, Compt. rend. 1909, **149**, 250; abst. J. C. S. 1909, **96**, ii, 721.
10. J. Duclaux, Compt. rend. 1905, **140**, 1544. Jour. Chim. Phys. 1907, **5**, 29, 40, 45; 1909, **7**, 413; Rev. gén. sci. 1910, **21**, 141; abst. J. C. S. 1905, **88**, ii, 511.
11. J. Perrin, Compt. rend. 1903, **137**, 564; Jour. Chim. Phys. 1904, **2**, 601; 1905, **3**, 50; abst. J. C. S. 1905, **88**, ii, 138.
12. O. Loew, Ber. 1887, **20**, 141, 3039; abst. J. S. C. I. 1887, **6**, 446;

M. Mercadante[1] is authority for the statement that the starch in cells of the medulla and medullary rays may be transformed into gum without any change of aspect or form, for he finds that gum appears in the cells contemporaneous with the starch, the latter occupying the center of the cellular mass, while the gum forms concentric layers outside of it in the interior of the cells.[2]

The behavior of starch as a protective colloid towards colloidal silver has been examined in detail by A. Gutbier and E. Weingaertner,[3] solutions obtained by reduction with hydrazine and with sodium hyposulfite being found similar in properties although the latter reacts more rapidly. According to this author the coagulating influence of electrolytes diminishes in the order: sulfuric acid, barium chloride, magnesium sulfate, ammonium carbonate, sodium hydroxide in the case of the solutions reduced by hydrazine; and barium chloride, sulfuric acid, magnesium sulfate, sodium carbonate and sodium hydroxide for solutions reduced by sodium hyposulfite.

In general, those electrolytes which accelerate the ageing of starch solutions increase the rate of coagulation, while those which retard the coagulation of pure starch solutions have a similar influence on silver starch solutions. The protective action of starch solution prepared at 100° and at 120° is practically the same, although the stability of dilute silver solutions is somewhat greater from starch solutions obtained at the higher temperature.

E. Jentys[4] considers the substance of starch grains to consist of a mixture of colloids composed of reducing sugar and aromatic substances related to the tannins but glucosidic in character. The stratified starch grains present in chloraplastids, leucaplastids, etc., are of varying composition in different portions of the

---

J. C. S. 1887, **52**, 459; Jahr. Chem. 1887, **40**, 2247. Bull. Soc. Chim. 1888, **49**, 712. See also C. Wehmer and B. Tollens, Ber. 1886, **19**, 2134, 2614. Ann. 1888, **243**, 334.

[1] Gazz. chim. ital. 1876, **6**, 97; abst. J. C. S. 1877, **31**, 104; Ber. 1876, **9**, 581; Jahr. Chem. 1876, **29**, 866; Chem. News, 1876, **33**, 205.

[2] B. Tollens, Ber. 1886, **19**, 2134; abst. J. C. S. 1886, **50**, 1006; Jahr. Chem. 1886, **39**, 1621.

[3] Koll. Chem. Beih. 1913, **5**, 211; abst. J. C. S. 1913, **104**, ii, 1034; C. A. 1914, **8**, 1225; J. S. C. I. 1914, **33**, 46; Chem. Zentr. 1914, **85**, I, 1333.

[4] Bull. Akad. Sci. Cracow, 1907, 203; abst. J. C. S. 1907, **92**, i, 589; abst. C. A. 1907, **1**, 2313; J. C. S. 1907, **92**, i, 589; Chem. Zentr. 1907, **78**, II, 687; Jahr. Chem. 1905–1908, II, 933.

granules. Stratification is the result of separation from a liquid mixture of carbohydrates and tannin-like substances. O. Treboux,[1] in his experiments with numerous varieties of Pomoidea, Prunoidea and Spiraeoidea has shown that all of them are able to produce starch from sorbitol. None of these plants, however, are able to utilize mannitol and dulcitol as compared with sugars and glycerol, the production of starch from sorbitol being always much more vigorous.

According to V. Griessmayer,[2] the coating surrounding the starch granules does not consist of a compound present in the unaltered granule, but is the result of change of the starch. This substance may be obtained by the action of acid pepsin on starch and is convertible into dextrin and finally into saccharine compounds. This amylodextrin is separable with difficulty unless it crystallizes in sphaero-crystals, these crystals acting on polarized light in the same manner as starch crystals, only the dark cross is diagonal rather than orthogonal.

In studying the changes in starch granules during germination, R. Whymper[3] made longitudinal sections of wheat grains through the embryo or germ, and transversely through the middle of the grain. Microscopical examinations of the moistened sections were made periodically, and the following conclusions arrived at. There appears to be no general relation between the size of starch granules and the ease with which they are attacked by diastase; although with mineral acids and wet and dry heat, almost invariably the larger granules of any one starch succumb more quickly to attack than smaller granules of the same kind.

In studying the formation of starch by mould fungi, F. Boas[4] found in experiments with *Aspergillus niger* and *Penicillium glaucum* cultivated in solutions of sucrose, dextrose, levulose, or dextrin containing ammonium salts, the liquid after some time acquired the property of yielding with iodine a blue coloration which

---

[1] Ber. deut. Bot. Ges. 1909, **27**, 428, 507; abst. J. C. S. 1910, **98**, ii, 61; Chem. Zentr. 1909, **80**, II, 1479; 1910, **81**, I, 189; Jahr. Chem. 1909, **62**, II, 370.

[2] Ann. 1871, **160**, 40; Bied. Centr. 1887, **16**, 190; abst. J. C. S. 1872, **25**, 72; 1887, **52**, 686; Chem. News, 1879, **40**, 180; J. S. C. I. 1887, **6**, 446.

[3] Seventh Intl. Cong. Appl. Chem. 1909; abst. J. S. C. I. 1909, **28**, 806; Zts. ang. Chem. 1909, **22**, 1248; C. A. 1910, **4**, 1821.

[4] Woch. Brau. 1917, **34**, 47; abst. Biochem. Zts. 1917, **78**, 308; J. S. C. I. 1917, **36**, 1285; C. A. 1917, **11**, 2216, 2816.

vanished on warming. The substance colored blue by iodine was also observed in the mycelial cell walls of the moulds. Under the influence of diastase the liquids lost their power of reacting with iodine. Alcohol precipitated the starch-like substance from solution in a flocculent form. The formation of this substance is attributed to the influence of a free acid liberated in consequence of the assimilation of the nitrogen of the ammonium salts by the moulds, for similar results were obtained in sugar solutions and in beer wort treated with free tartaric, phosphoric, or sulfuric acids.

Occurrence of Starch. At some period of growth starch is present in all plants, and is said to be found in most of the parts. It is found in larger amounts in some families than in others, being especially abundant in the seeds of all the Leguminosae, in the stems of various species of Sagus and Cycas, in the roots of many plants of the natural orders Euphorbiaceae and Zinziberaceae, and in the tubers of the potato, artichoke, cassava and canna.

Starch is especially found as a reserve material stored up in the seeds, pith and stems, but it is still a debatable question as to whether the starch found in the leaves, sap and those portions of the plant outside the "reserve organs," is identical with the starch of these organs. Certain microchemical reactions would indicate there is a difference.

Starch is also found in varying amounts in the same parts of the plant at different periods of the 24 hours. In general, it occurs in the green leaves and associated with chlorophyl with which it is intimately identified during the day time, the proportion varying as to the climatic conditions of the particular day, especially the intensity of the sunlight and the moisture present in the atmosphere. It appears to be present in largest amounts toward the close of the day, and is at a minimum in the morning. Abundant evidence has accumulated that at night the starch undergoes a transformation into a dialyzable or soluble form, and in this condition is transported from one part of the plant to the other. Whether this soluble form is a sugar has not been definitely ascertained.

Starch has also been found in the pith of shrubs and in lignocellulose tissue, but whether present here in a transitory condition or as a permanent resting place is not clear. Although starch is not known to be an animal product, there appears, in certain pathological processes, to be a relation between starch and glycogen, especially in the liver. It is present in some fungi.[1]

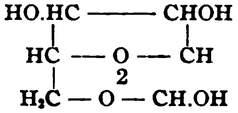
Molecular Weight of Starch. The absolute molecular weight of starch is unknown, but undoubtedly is very high. Representing the formula as $(C_6H_{10}O_5)n$, according to H. Brown and G. Morris[2] by the use of Raoult's method of molecular weights determination, n is 200 for soluble starch, i. e., it has a molecular weight of 32400. T. Pfeiffer and B. Tollens[3] arrive at the value of $n = 2$, obtained from the composition of some sodium and potassium salts. The investigations of C. O'Sullivan[4] lead to the conclusion that n is not less than 72. Independently, R. Sachsse[5] and W. Naegeli[6] have proposed $6n + H_2O$ as the formula, while F. Mylius,[7] Salomon,[8] and others,[9] have arrived at different formulas. According to O'Sullivan,[10] we may be assured that the

---

1. E. Bourquelot, J. Pharm. Chim. 1891, (5), **24**, 197; abst. J. C. S. 1892, **62**, 230.
2. Chem. News, 1888, **57**, 196; J. C. S. 1889, **55**, 462; abst. Bull. Soc. Chim. 1890, **4**, 731; Ber. 1888, **21**, R, 595; 1891, **24**, R, 723; Chem. Centr. 1889, **60**, II, 122, 285; Jahr. Chem. 1888, **41**, 119; 1889, **42**, 136.
3. Ann. 1881, **210**, 295; Bied. Centr. 1882, **11**, 775; abst. J. C. S. 1883, **44**, 307; Chem. News, 1882, **45**, 78; Bull. Soc. Chim. 1882, **38**, 206; Jahr. Chem. 1881, **34**, 980.
4. J. C. S. 1879, **35**, 783; Chem. News, 1879, **40**, 236, 288; abst. Bull. Soc. Chim. 1879, **32**, 493; Jahr. Chem. 1879, **32**, 845.
5. Leipziger naturf. Ges. Ber. 1877, 30; abst. Chem. News, 1879, **39**, 264; Chem. Centr. 1877, **48**, 732; Chem. Tech. Rep. 1878, **17**, I, 297; Jahr. Chem. 1877, **30**, 898; Jahr. rein Chem. 1877, **5**, 175; Zts. Chem. Grossgew. 1877, **2**, 588.
6. Ann. 1874, **173**, 218; abst. Chem. News, 1874, **30**, 229; J. C. S. 1875, **28**, 55; Poly. Centr. 1874, **40**, 1297; Chem. Centr. 1874, **45**, 809; Jahr. Chem. 1874, **27**, 878; Jahr. rein Chem. 1874, **2**, 176; Wag. Jahr. 1874, **20**, 653.
7. Ber. 1887, **20**, 694; abst. J. C. S. 1887, **52**, 568; J. S. C. I. 1887, **6**, 563; Bull. Soc. Chim. 1887, **48**, 461; Jahr. Chem. 1887, **40**, 2263. L. Wacker, Ber. 1908, **41**, 266; 1909, **42**, 2675; abst. J. S. C. I. 1909, **28**, 898; Chem. News, 1908, **97**, 143; J. C. S. 1908, **94**, i, 135; 1909, **96**, i, 633; Chem. Zentr. 1908, **79**, I, 989; 1909, **80**, II, 567; Jahr. Chem. 1905–1908, II, 840. Cf. J. Traube, Ber. 1897, **30**, 272.
8. Ber. 1883, **16**, 2509; J. prakt. Chem. 1883, **136**, 82; abst. J. C. S. 1884, **46**, 36; Bull. Soc. Chim. 1884, **42**, 292; Jahr. Chem. 1883, **36**, 1366.
9. V. Syniewski, Ann. 1900, **309**, 282; 1902, **324**, 212, 260; abst. J. C. S. 1903, **84**, i, 68, 69; J. S. C. I. 1902, **21**, 1341; Jahr. Chem. 1902, **55**, 1034. H. Rodewald, Zts. physik. Chem. 1897, **24**, 193; 1900, **33**, 593; abst. J. C. S. 1898, **74**, ii, 61; 1900, **78**, i, 477; Bull. Soc. Chim. 1898, **20**, 4; Chem. Centr. 1897, **68**, II, 1068; 1900, **71**, II, 180; Jahr. Chem. 1897, **50**, 189; 1900, **53**, 830. C. Lintner and G. Düll, Chem. Ztg. 1893, **17**, 1340; Ber. 1893, **26**, 2533; abst. J. C. S. 1894, **66**, i, 5; J. S. C. I. 1894, **13**, 53; Bull. Soc. Chim. 1894, **12**, 439; Chem. Centr. 1894, **65**, I, 22; Jahr. Chem. 1893, **46**, 891.
10. Thorpe Dict. Chem. 1914, **5**, 155, 161, 165.

molecular weight of starch is certainly not less than $C_{240}H_{400}O_{200}$.

J. Sarasin[1] has made careful examination of the products of decomposition of cellulose and starch by heat, the results obtained indicating that *l*-glucosan is an intermediate product in the breaking down process and that this material when distilled under reduced pressure gives the same products as do starch and cellulose. These two compounds are thus considered to be polymerides of *l*-glucosan, to which the author ascribes the following formula:



and he considers that it is the ring 2 which opens, giving two free valences for the polymerization, since among the products of decomposition of starch and cellulose 2:5-dimethylfurfuran is found.

By the action of heated malt extract upon starch, V. Syniewski found[2] that starch solution after 216 hours was converted into a product like the maltodextrin of Brown and Morris, achroodextrin II of Lintner, and the maltodextrin of Ling and Baker. The author calls this "Grenzdextrin II," of a molecular formula $C_{36}H_{62}O_{31}$. In the carbinol hydrolysis of starch, amylodextrin results on heating starch paste in an autoclave at 140°. This author assumes that nine glucose residues make up the amylogen complex $C_{54}H_{90}O_{45}$ of starch are connected by nine carbonyl linkages of three different kinds, viz., three α-linkages connecting the three maltose residues to a central Grenzdextrin I. (C_{18}) residue, three β-linkages which connect the three glucose components of this Grenzdextrin I residue, and three γ-linkages which connect the glucose components of the three maltose residues.

The potato-starch molecule is regarded as being made up of four amylogen complexes, and its formula is $C_{216}H_{360}O_{180}$. In this molecule each amylogen complex is connected with the others by six carbinol anhydride linkages, three operating between Grenzdextrin I. residues (*d*-carbinol bonds), and three between maltose residues (*m*-carbinol bonds). The malto-carbinol bonds are hydrolyzed by heatng with water at 140°; all other hydrolyzes, with

---

[1] Arch. Sci. phys. nat. 1918, (4), **46,** 5; abst. J. C. S. 1918, **114,** i, 375; C. A. 1918, **12,** 2187.

[2] Ann. 1902, **324,** 212; abst. J. S. C. I. 1902, **21,** 1341; Bull. Acad. Sci. Cracow, 1902, 441; J. C. S. 1903, **84,** i, 69; Jahr. Chem. 1902, **55,** 1034.

malt extracts in different ways, act upon the various carbonyl linkages. The two (C_{18}) components of Grenzdextrin II. and the two glucose components of dextrinose are united by the *d*-carbinol bonds, and these resist to the end.

Starch Iodide. The so-called "iodide" of starch has been the subject of much investigation and considerable controversy. Since its discovery by F. Stromeyer,[1] an unusually extensive literature has arisen, N. Blondlot,[2] A. Bechamp,[3] J. Pohl,[4] R. Fresenius,[5] É. Duclaux,[6] B. Brukner,[7] F. Kuester,[8] V. Griessmayer,[9] J. Personne[10] and É. Baudrimont,[11] consider it to be a mixture of starch with iodine or a solution of the latter in the former, while É. Rouvier,[12] A. Payen,[13] J. Fritzsche,[14] L. Bondon-

---

[1] Thorpe, Dict. Chem. 1914, **5**, 158. Gilb. Ann. 1815, **49**, 146.

[2] Ann. Chim. Phys. 1855, (3), **43**, 225; abst. J. pharm. chim. 1855, **28**, 45; Jahr. Chem. 1855, **8**, 679. See Leroy and Raspail, Schw. Jour. 1833, **68**, 179.

[3] J. pharm. chim. 1855, (3), **27**, 406; **28**, 303; Jahr. Chem. 1855, **8**, 679. Bull. Soc. Encour. 1862, 187; abst. Dingl. Poly. 1862, **165**, 67; Jahr. Chem. 1862, **15**, 577; Zts. anal. Chem. 1862, **1**, 466; Chem. Tech. Rep. 1862, **1**, II, 89.

[4] J. prakt. Chem. 1861, **83**, 38; Zts. anal. Chem. 1862, **1**, 84; Jahr. Chem. 1861, **14**, 715.

[5] Ann. 1857, **102**, 184; Zts. anal. Chem. 1862, **1**, 84.

[6] Compt. rend. 1872, **74**, 533; Ann. Chim. Phys. 1872, (4), **25**, 264; Abst. J. C. S. 1872, **25**, 299, 687; Jahr. Chem. 1872, **25**, 770. See "Traite de Microbiologie," 1899, **2**, Chapt. 15, 22–25.

[7] Monatsh. Chem. 1883, **4**, 889, 906; abst. J. C. S. 1884, **46**, 575; J. Pharm. chim. 1885, (5), **12**, 236.

[8] Ann. 1895, **283**, 360, 376; Ber. 1895, **28**, 783; abst. J. C. S. 1895, **68**, i, 199; Bull. Soc. Chim. 1895, **14**, 704; Ber. 1895, **28**, R, 280; Jahr. Chem. 1895, **48**, 514, 515.

[9] Ann. 1871, **160**, 40; abst. Chem. News, 1871, **24**, 265; J. C. S. 1872, **25**, 272; Bull. Soc. Chim. 1872, **17**, 60; Chem. Centr. 1871, **42**, 636; Jahr. Chem. 1871, **24**, 789. See also Zts. f. ges. Br. 1878, 394. J. prakt. Chem. 1893, **156**, 225; abst. J. C. S. 1893, **64**, i, 684; Ber. 1893, **26**, R, 801; Chem. Centr. 1893, **64**, II, 681; Jahr. Chem. 1893, **46**, 894.

[10] Bull. Soc. Chim. 1861, **3**, 71; J. pharm. chim. 1861, (3), **39**, 49. Bull. Soc. Chim. 1866, **5**, 454; J. pharm. chim. 1866, (4), **3**, 94. Compt. rend. 1872, **74**, 617; abst. Jahr. Chem. 1872, **25**, 771.

[11] Compt. rend. 1860, **51**, 825; Bull. Soc. Chim. 1860, (1), **1**, 246; abst. Rep. Chim. appl. 1860, **2**, 392; Mon. Sci. 1861, **3**, 266; Jahr. Chem. 1860, **13**, 501; Zts. Chem. 1861, 27.

[12] Compt. rend. 1892, **114**, 128, 749, 1366; 1893, **117**, 281, 461; 1894, **118**, 743; 1895, **120**, 1179; 1897, **124**, 565; abst. J. C. S. 1892, **62**, 578, 801, 1171; J. S. C. I. 1897, **16**, 475; Jahr. Chem. 1892, **45**, 2468; 1893, **46**, 893; 1894, **47**, 1338; 1895, **48**, 197; 1897, **50**, 1516.

[13] Compt. rend. 1865, **61**, 512; Ann. Chim. Phys. 1865, (4), **4**, 286; Bull. Soc. Chim. 1865, **3**, 470; abst. Chem. Centr. 1865, **36**, 845; Jahr. Chem. 1865, **18**, 597.

[14] Pogg. Ann. 1834, **32**, 129; Ann. 1834, **12**, 287.

neau,[1] P. Guichard,[2] E. Sonstadt,[3] H. Pellet,[4] E. Schär,[5] T. Gobley,[6] F. Goppelsroeder,[7] C. Harz[8] and H. Friedenthal[9] consider it to be a chemical compound of starch and iodine. The amount of iodine found has varied all the way from 3.2% to 19.6%, and formulas deduced varying over a correspondingly wide range.

F. Kuester has shown[10] that the amount of halogen in starch iodide varies continuously with the concentration of the iodine solution with which it is in equilibrium, and, rejecting the formulas of F. Mylius,[11] H. Friedenthal,[12] considers the blue substance to be a solid solution of iodine in starch. While Mylius maintains that the presence of hydriodic acid or an iodide is not

---

1. Compt. rend. 1877, **85**, 671, 673; Bull. Soc. Chim. 1877, (2), **28**, 452; abst. J. C. S. 1878, **34**, 22; Chem. News, 1877, **36**, 195; J. pharm. chim. 1878, (4), **27**, 121; Jahr. Chem. 1877, **30**, 899. Other investigations in the starch group are, Compt. rend. 1875, **80**, 671; abst. J. C. S. 1875, **28**, 629. Compt. rend. 1884, **98**, 153; abst. J. C. S. 1884, **46**, 927. Dingl. Poly. 1874, **213**, 172. Bull. Soc. Chim. 1874, **21**, 147. Bull. Soc. Encour. 1893, 849; abst. J. S. C. I. 1894, **13**, 750. Rep. anal. Chem. **14**, 222; abst. J. S. C. I. 1885, **4**, 541.

The Bondonneau feculometer is described in Dingl. Poly. 1874, **212**, 172; abst. J. C. S. 1875, **28**, 385. V. Bondonneau and A. Foret, E. P. 986, 1887; abst. J. S. C. I. 1888, **7**, 335. D. R. P. 42519; abst. Ber. 1888, **21**, R, 335; Wag. Jahr. 1888, **34**, 848.

2. Rep. Chim. Pure, 1863, **5**, 115, 278; abst. Chem. Centr. 1863, **34**, 844; Jahr. Chem. 1863, **16**, 569. See M. Guichard. Chem. News, 1868, **18**, 6.

3. Chem. News, 1873, **28**, 248; abst. J. C. S. 1874, **27**, 352; Amer. Chemist, 1874, **4**, 396; Jahr. Chem. 1873, **26**, 828; Jahr. rein chem. 1873, **1**, 115.

4. Bull. Soc. Chem. 1867, **7**, 147; Mon. Sci. 1877, **19**, 988; abst. Chem. Centr. 1867, **38**, 1008; Zts. Chem. 1867, 352; Jahr. Chem. 1867, **20**, 838; 1877, **30**, 898.

5. Pharm. Centralh. 1896, **37**, 540; abst. J. C. S. 1897, **72**, 454; Ber. 1896, **29**, R, 1157; Chem. Centr. 1896, **67**, II, 661; Deut. Chem. Ztg. 1896, **11**, 355; Jahr. Chem. 1896, **49**, 1023.

6. Dingl. Poly. 1844, **92**, 128; J. Chim. med. 1844, **10**, 121; J. pharm. chim. 1844, (3), **5**, 299; Annuaire de chim. 1845, **1**, 315.

7. Pogg. Ann. Phys. 1863, **109**, 57; abst. Jahr. Chem. 1863, **16**, 670; Rep. Chim. Pure, 1863, **5**, 615; Zts. anal. Chem. 1863, **2**, 157; Vierteljahrschr. prakt. Pharm. **13**, 236.

8. Alcohol, 1898, 116; abst. Chem. Ztg. Rep. 1898, **22**, 86; Chem. Centr. 1898, **69**, I, 1018; Jahr. Chem. 1898, **51**, 1355.

9. Centr. Physiol. 1899, **12**, 849; abst. Chem. Centr. 1899, **70**, I, 924; J. C. S. 1899, **76**, i, 851; Jahr. Chem. 1899, **52**, 1271.

10. Ann. 1895, **283**, 360, 376; Ber. 1895, **28**, 783; abst. J. C. S. 1895, **68**, i, 199; Bull. Soc. Chim. 1895, **14**, 704; Ber. 1895, **28**, R, 280; Jahr. Chem. 1895, **48**, 514, 515.

11. Ber. 1887, **20**, 688; 1895, **28**, 385; Zts. physiol. Chem. 1887, **11**, 306; abst. J. C. S. 1887, **52**, 568; J. S. C. I. 1887, **6**, 563; Bull. Soc. Chim. 1887, **46**, 461; Jahr. Chem. 1887, **40**, 2263.

12. Centr. Physiol. **12**, 849; Chem. Centr. 1899, **70**, I, 924; J. C. S. 1899, **76**, i, 851; Jahr. Chem. 1899, **52**, 1271.

essential to the formation of starch iodide, F. Seyfert,[1] J. Toth,[2] F. Hale[3] and H. Stocks[4] contend HI or an alkaline iodide is essential, as well as small amounts of water.

If starch and iodine chemically unite, the compound is readily dissociated,[5] and for this reason chemists have preferred to employ physico-chemical methods, such as depression of the freezing point;[6] osmotic pressure measurement of starch iodide;[7] vapor pressure of iodine in starch solutions and the partial coefficient of iodine between starch solutions and chloroform;[8] electric conductivity;[9] while M. Katayama[10] used a tintometric method.

Analogous to the blue color produced by starch with iodine, are cholalic acid[11] and lanthanum acetate,[12] while the blue color is

---

1. Zts. ang. Chem. 1888, **1**, 15, 126; abst. J. C. S. 1888, **54**, 1050, 1134; J. S. C. I. 1888, **7**, 350; 1889, **8**, 295; Ber. 1888, **21**, R, 298; Chem. Centr. 1888, **59**, 324, 502; Chem. Ind. 1888, **11**, 159; Chem. Ztg. Rep. 1888, **12**, 30; Jahr. Chem. 1888, **41**, 2577, 2578; Wag. Jahr. 1888, **34**, 839, 840. Cf. also A. v. Asboth, Chem. Ztg. 1887, **11**, 785; abst. J. C. S. 1887, **52**, 868; J. pharm. chim. 1888, (5), **17**, 116; J. S. C. I. 1887, **6**, 608; Ber. 1887, **20**, R, 483; Chem. Tech. Rep. 1887, **26**, II, 330; Jahr. Chem. 1887, **40**, 2464.

2. Chem. Ztg. 1891, **15**, 1523, 1583; abst. Jahr. Chem. 1891, **44**, 2179.

3. Amer. J. Sci. (Silliman), 1902, **163**, 379; Amer. Chem. J. 1902, **28**, 438; abst. J. S. C. I. 1902, **21**, 1040; J. C. S. 1902, **82**, i, 533; 1903, **84**, i, 151; Bull. Soc. Chim. 1902, **30**, 325; Chem. Centr. 1902, **73**, II, 26; Jahr. Chem. 1902, **55**, 243, 1038; Zts. anorg. Chem. 1902, **31**, 100.

4. Chem. News, 1887, **56**, 212; 1888, **57**, 183; abst. J. C. S. 1888, **54**, 126, 668; Ber. 1888, **21**, R, 479; Chem. Tech. Rep. 1887, **26**, II, 280; Chem. Ind. 1888, **11**, 159.

5. G. Barger and E. Field, J. C. S. 1912, **101**, 1394; abst. C. A. 1913, **7**, 330; Bull. Soc. Chim. 1913, **14**, 3; Chem. Zentr. 1912, **83**, II, 1520; Chem. Ztg. 1912, **36**, 1240.

6. H. Friedenthal, Centr. Physiol. 1899, **13**, 54; abst. J. C. S. 1899, **76**, i, 851; Chem. Centr. 1899, **70**, I, 924; Jahr. Chem. 1899, **52**, 1271.

7. H. Rodewald and A. Kattein, Sitzber. preuss. Akad. Wiss. 1899, 628; Zts. physik. Chem. 1900, **33**, 586; abst. J. C. S. 1900, **78**, i, 79, 477; J. S. C. I. 1899, **18**, 1062; Chem. Centr. 1899, **70**, II, 419; 1900, **71**, II, 180; Jahr. Chem. 1899, **52**, 1271; 1900, **53**, 829.

8. L. Andrews and H. Goettsch, J. Amer. Chem. Soc. 1902, **24**, 865; abst. J. C. S. 1903, **84**, i, 10; Chem. Centr. 1902, **73**, II, 1035; Rep. Chim. 1902, **2**, 422; Jahr. Chem. 1902, **55**, 1037.

9. M. Padoa and B. Savare, Gazz. chim. ital. 1906, **36**, i, 313; Atti R. Acad. Lincei, 1905, (5), **14**, i, 467; abst. J. C. S. 1905, **88**, i, 416; Bull. Soc. Chim. 1906, **36**, 760; Chem. Centr. 1906, **77**, II, 108; Jahr. Chem. 1905–1908, II, 946.

10. Zts. anor. Chem. 1907, **56**, 209; abst. J. S. C. I. 1907, **26**, 1289; C. A. 1908, **2**, 749; J. C. S. 1908, **94**, i, 9; Chem. Zentr. 1908, **79**, I, 239; Jahr. Chem. 1905–1908, I, 1496.

11. F. Mylius, Ber. 1887, **20**, 683; 1895, **28**, 388; abst. J. C. S. 1887, **52**, 606, 982; 1895, **68**, i, 313; Bull. Soc. Chim. 1887, **48**, 461; 1888, **49**, 58, 834; 1895, **14**, 901; Chem. Centr. 1887, **58**, 539; 1895, **66**, I, 793; Jahr. Chem. 1887, **40**, 2333; 1895, **48**, 514.

12. F. Kuester, Zts. physik. Chem. 1895, **16**, 156; abst. J. C. S. 1895, **68**, i, 313, 322; Bull. Soc. Chim. 1898, **16**, 649; Ber. 1895, **28**, 720, 783; Chem.

inhibited or modified by the presence of chloral hydrate,[1] tannin,[2] many phenols,[3] egg albumen[4] and acacia or malt extract or silver nitrate.[5] W. Harrison[6] considers that in the case of starch an adsorption compound is formed similar to the purple of Cassius, and attempted to prepare colloidal blue iodine solutions. C. Tomlinson[7] states that on heating iodide of starch, in all cases the blue color disappears at the temperature of boiling water, although according to S. Pickering[8] the temperature at which the color disappears varies with the intensity it possessed before heating. A. Clementi[9] finds that the velocity of decoloration is proportional to the amount of furfural liberated, and inversely proportional to the amount of iodine present, and that the decoloration is aided by the presence of certain proteins such as albumins, globulins, albuminates and phosphoproteins. Starch iodide may also be produced by means of iodine monochloride or iodine monobromide.[10]

In the presence of a metallic iodide, starch is colored blue by a much smaller quantity of iodine, than when iodides are absent.[11] In fact, an aqueous solution of iodine may be added to a solution of starch until the liquid is yellowish without the

---

Centr. 1895, **66**, I, 656, 1113; Jahr. Chem. 1895, **48**, 514, 515. W. Biltz, Ber. 1904, **37**, 719; abst. J. C. S. 1904, **86**, II, 339; Bull. Soc. Chim. 1904, **32**, 1235; Chem. Centr. 1904, **75**, I, 1001; Jahr. Chem. 1904, **57**, 98.

[1] E. Schaer, Pharm. Centralh. 1896, **37**, 540; abst. J. C. S. 1897, **72**, i, 454; Ber. 1896, **29**, R, 1157; Chem. Centr. 1896, **67**, II, 661; Deut. Chem. Ztg. 1896, **11**, 355; Jahr. Chem. 1896, **49**, 1023.

[2] E. Heintz, Jahr. Agri. Chem. 1879, 499.

[3] Such as pyrocatechin, hydrochinon, resorcin, pyrogallol, but not phenol.

[4] E. Puchot, Ber. 1876, **9**, 1472; Compt. rend. 1876, **83**, 225; abst. J. C. S. 1877, **31**, 107; Chem. News, 1876, **34**, 72; Bull. Soc. Chim. 1877, **27**, 138; Jahr. Chem. 1876, **29**, 1032; Zts. anal. Chem. 1876, **15**, 460.

[5] Amer. J. Sci. 1894, **147**, 422; abst. J. C. S. 1894, **66**, i, 398; Chem. Centr. 1894, **65**, II, 147; Ber. 1894, **27**, R, 602; Jahr. Chem. 1894, **47**, 105.

[6] J. Soc. Dyers Col. 1911, **27**, 84; 1916, **32**, 40; Chem. Soc. Proc. 1910, **26**, 252; abst. J. C. S. 1916, **109**, i, 251; J. S. C. I. 1910, **29**, 1335; 1911, **30**, 534; 1916, **35**, 321; C. A. 1911, **5**, 2769; 1912, **6**, 18.

[7] Phil. Mag. 1885, (5), **20**, 168; abst. J. C. S. 1886, **50**, 328.

[8] Chem. News, 1880, **42**, 311; Zts. anal. Chem. 1882, **21**, 125; Jahr. Chem. 1880, **33**, 1214.

[9] Arch. Farm. Sperim. 1915, **20**, 258; abst. J. C. S. 1916, **110**, ii, 400; J. S. C. I. 1916, **35**, 909; C. A. 1916, **10**, 67.

[10] H. Beckurts and W. Freytag, Pharm. Centralh. 1886, **27**, 231; Chem. Centr. 1886, 454; J. C. S. 1886, **50**, i, 783; Ber. 1886, **19**, R, 415; Chem. Ind. 1887, **10**, 27; Chem. Tech. Rep. 1886, **25**, II, 332; Jahr. Chem. 1886, **39**, 1911; Wag. Jahr. 1886, **32**, 302.

[11] C. Lonnes, Zts. anal. Chem. 1894, **33**, 409; abst. J. C. S. 1894, **66**, ii, 475; Ber. 1895, **28**, R, 27; Jahr. Chem. 1894, **47**, 104.

development of any blue color.[1] The addition of a very small amount of KI, however, will induce the reaction Solutions of starch in zinc chloride or other chloride, upon standing do not respond to this reaction, the starch meanwhile having been converted into dextrin.[2]

As A. Lachmann has observed,[3] the purity of the solvent modifies the color and the sensibility of the reaction to a considerable extent. According to N. Castoro,[4] amylopectin reacts blue with iodine in the same manner as starch. The recent work of H. Bordier[5] has shown that sunlight exerts a powerful decolorizing action on starch iodide, and suggests the explanation lies in the conversion of I to HI under the influence of sunlight.

In a critical investigation of the subject, L. Berczeller[6] shows that KI is not necessary for the formation of the starch-I complex, whose inhibition temperature is about one degree above that of pure starch, and that starch takes up more iodine at a lower than at a higher temperature. The adsorption equilibrium between starch and iodine takes place more rapidly in dilute than in concentrated solutions.

When an excess of iodine is added to starch paste in the presence of a large quantity of water, the iodide of starch separates as a dark colored powder, which upon washing out with water and drying, gives an amorphous metallic appearing powder. In the dry condition it is stable.

Starch iodide is precipitated from solutions by means of strong acids,[7] which in the presence of various salts assumes different

[1] C. Meineke, Chem. Ztg. 1894, **18**, 157; abst. Chem. Centr. 1894, **65**, I, 525; Chem. News, 1894, **69**, 241; J. C. S. 1895; **68**, i, 79; Ber. 1894, **27**, R, 205; Chem. Tech. Rep. 1894, **33**, I, 286; Jahr. Chem. 1894, **47**, 2402.

[2] F. Musset, Pharm. Centralh. 1896, **37**, 587; Chem. Centr. 1896, **67**, II, 703; abst. J. C. S. 1897, **72**, i, 455; Jahr. Chem. 1896, **49**, 1024; Wag. Jahr. 1896, **42**, 774.

[3] J. A. C. S. 1903, **25**, 50; abst. J. C. S. 1903, **84**, ii, 283; Chem. News, 1903, **88**, 307; Rep. Chim. 1903, **3**, 121; Chem. Centr. 1903, **74**, I, 617; Jahr. Chem. 1903, **56**, 324.

[4] Gazz. chim. ital. 1909, **39**, i, 603; abst. J. C. S. 1909, **96**, i, 634; C. A. 1911, **5**, 619; J. S. C. I. 1909, **28**, 898; Rep. Chim. 1910, **10**, 40; Chem. Zentr. 1909, **80**, II, 974; Jahr. Chem. 1909, **62**, II, 374.

[5] Compt. rend. 1916, **163**, 205, 291; abst. J. C. S. 1916, **110**, i, 630; J. S. C. I. 1916, **35**, 962; C. A. 1916, **10**, 2669; 3016; Mon. Sci. 1916, **83**, 239.

[6] Biochem. Zts. 1917, **84**, 37, 106; abst. J. C. S. 1918, **114**, i, 101, 131; J. S. C. I. 1918, **37**, 133-A; C. A. 1918, **12**, 1264.

[7] See G. Kruess and E. Thiele, Zts. anor. Chem. 1894, **7**, 52; abst. J. C. S. 1894, **66**, ii, 445; Chem. News, 1894, **70**, 197; Ber. 1894, **27**, R, 719; Chem. Centr. 1894, **65**, II, 580; Jahr. Chem. 1894, **47**, 392. A. Meyer, Bot. Ztg. 1895, 23. J. Gruess, Jahr. wiss. Mikr. 1896, **26**, 379.

colors[1] and is colored yellow by bromine,[2] which color, however, may be washed out by water. On account of its strong disinfectant properties, starch iodide has been proposed[3] as a topical application to wounds. It is also alleged to possess strong bactericidal properties.

Starch iodide paper—made by soaking filter paper in starch solution containing an iodide—has been used to detect ozone.[4] C. Storm[5] has given a method for its preparation.

Starch Esters. Of the organic esters of starch, the formate and acetate appear to be fairly definitely characterized. As described by J. Traquair,[6] starch formate is a white powder, sub-

---

[1] A. Vogel, N. Rep. Pharm. 1873, **22**, 349; abst. Jahr. Chem. 1873, **26**, 829; J. C. S. 1874, **27**, 708; Bull. Soc. Chim. 1873, **20**, 492. Cf. J. Pharm. Chim. 1865, (4), **2**, 72.

[2] For additional information consult, C. van Deventer, Chem. Centr. 1888, **59**, 424. Pohl, J. prakt. chem. 1861, **83**, 35; abst. Jahr. Chem. 1861, **14**, 716. Vogel, Jahr. Chem. 1873, **26**, 829. J. Duroy, Compt. rend. 1860, **51**, 1031; J. pharm. chim. 1861, **39**, 94. B. Bruckner, Monatsh. 1883, **4**, 889, 906; abst. J. C. S. 1884, **46**, 576; Akad. Wien. 1883, **88**, Pt. 1. Schoenbein, Jahr. Chem. 1861, **14**, 716. Guichard, Jahr. Chem. 1863, **16**, 569. Tomlinson, Phil. Mag. 1885, **20**, 168. Goppelsroeder, Jahr. Chem. 1863, **16**, 670. Fresenius, Ann. 1857, **102**, 184. Mylius, Ber. 1887, **20**, 691; Proc. Chem. Soc. 1910, **26**, 252. H. Geubel, Jahr. pr. Pharm. 1852, **24**, 337; abst. Jahr. Chem. 1852, **5**, 657. Blondonneau, Bull. Soc. Chim. **28**, 452. Duclaux, Zts. Chem. 1871, **7**, 702. Seifert, Jahr. Tierchem. 1888, **18**, 21. Rouvier, Ber. 1892, **25**, 501; Compt. rend. 1897, **124**, 565. Fritzsche, Ann. 1834, **12**, 287. A. Girard, Ann. Chim. Phys. 1887, (6), **12**, 275. Pickering, Zts. anal. Chem. 1882, **21**, 125. Mylius, Ber. 1893, **28**, 389. Kuester, Ann. 1894, **283**, 370. Friedenthal, Chem. Centr. 1899, **70**, I, 1162. R. Kemper, Archiv. d. Pharm. 1862, **162**, 253; abst. Jahr. Chem. 1863, **16**, 571. Franchimont, Rec. Trav. Pays-Bas. 1883, **2**, 92. J. Lassaigne, Ann. Chim. Phys. 1833, (2), **53**, 109; Jour. Chim. med. 1851, (3), **7**, 180. C. Lownes, Zts. anal. Chem. 1894, **33**, 409. M. Magnes-Lahrens, J. pharm. chim. 1849, (3), **19**, 243; 1851, (3), **21**, 13. C. Naegeli, Instit. 1863, 263. F. Pisani, Compt. rend. 1856, **43**, 1118; J. prakt. Chem. 1857, **70**, 382. A. Potilitzin, Ber. 1880, **13**, 2400; Jahr. Chem. 1880, **33**, 246. C. Schönbein, J. prakt. Chem. 1861, **84**, 385; Chem. Centr. 1862, **33**, 239. H. Rodewald and A. Kattein, Sitzungber. Akad. Wiss. Berlin, **24**, 628; Chem. Centr. 1899, **70**, II, 419; J. S. C. I. 1899, **18**, 1062. J. Soubeiran, J. pharm. chim. 1852, (3), **21**, 329. A. Vogel, N. Rep. Pharm. 1873, **22**, 349; 1875, **25**, 565.

[3] A. Lumiere, Compt. rend. 1917, **165**, 376; abst. J. S. C. I. 1917, **36**, 1061; C. A. 1918, **12**, 189.

[4] C. Daubeny, J. C. S. 1867, **20**, 1; Chem. News, 1866, **14**, 246; Brit. Assoc. Repts. 1866, 37; abst. Jahr. Chem. 1867, **20**, 181; Zts. anal. Chem. 1867, **6**, 208.

[5] C. Storm, J. Ind. Eng. Chem. 1909, **1**, 802; abst. J. S. C. I. 1910, **29**, 177; Chem. Zentr. 1910, **81**, I, 1806; C. A. 1910, **4**, 514. Boll. Chim. farm. 1914, **53**, 736; abst. C. A. 1916, **10**, 1970.

[6] J. S. C. I. 1909, **28**, 290; abst. Zts. ang. Chem. 1909, **22**, 2346; Bull. Soc. Chim. 1909, (4), **6**, 1152; Chem. Zentr. 1909, **80**, 1, 1987; C. A. 1909, **3**, 1602, 2070.

stantially soluble in water, and lacking the characteristic starch appearance,[1] as well as the typical chemical reactions.

Starch acetate[2] was first prepared in 1870,[3] and subsequently investigated by L. Schulze,[4] A. Michael,[5] Z. Skraup and H. Hamburger,[6] D. Law,[7] F. Pregl,[8] K. Zulkowsky,[9] J. Traquair,[10] C. Cross and E. Bevan,[11] A. Kldiaschwili,[12] and W. de Conick and A. Raynaud,[13] the organic esters of cellulose and starch being

1. Compare U. S. P. 778173, 1904; E. P. 9868, 1902; abst. J. S. C. I. 1903, **22**, 1008; J. Soc. Dyers, 1903, **19**, 275; Chem. Ztg. 1903, **27**, 862.
2. See E. Worden, Kunst. 1913, **3**, 61; abst. C. A. 1913, **7**, 1633; Zts. ang. Chem. 1913, **26**, II, 320.
3. Ann. Chim. Phys. 1870, (4), **21**, 235; abst. Chem. Centr. 1871, **42**, 568. Reproduced Ann. 1871, **160**, 74; abst. Chem. Centr. 1871, **42**, 740; J. C. S. 1872, **25**, 66.
4. J. prakt. chem. 1883, **136**, 324; abst. Chem. Centr. 1884, **55**, 217; Jahr. Chem. 1883, **36**, 1366; J. C. S. 1884, **46**, 284; Bull. Soc. Chim. 1884, **42**, II, 292; Jahr. Chem. 1883, **36**, 1366.
5. Amer. Chem. J. 1883–1884, **5**, 359; abst. J. C. S. 1884, **46**, 420; Bull. Soc. Chim. 1884, **42**, II, 354; Jahr. Chem. 1883, **36**, 1366.
6. Ber. 1899, **32**, 2413; abst. J. S. C. I. 1899, **18**, 941; Chem. Centr. 1899, **70**, II, 752; Jahr. Chem. 1899, **51**, 1288; J. C. S. 1908, **94**, 321.
7. Chem. Ztg. 1908, **32**, 365; abst. J. C. S. 1908, **94**, 321; Bull. Soc. Chim. 1909, (4), **6**, 157; Zts. ang. Chem. 1908, **21**, 1377; Chem. Zentr. 1908, **79**, I, 183; Jahr. Chem. 1905–1908, II, 55.
8. Wien. Akad. Ber. 1901, **110**, II-b, 881; Monatsh. Chem. 1901, **22**, 1049; J. C. S. 1902, **82**, 135; J. S. C. I. 1902, **21**, 129; Bull. Soc. Chim. 1902, (3), **28**, 929; Chem. Centr. 1902, **73**, I, 182; Jahr. Chem. 1901, **54**, 880.
9. Wien. Akad. Ber. 1880, **72**, II, 384; Ber. 1880, **13**, 1395; 1890, **23**, 3295; Chem. Centr. 1880, **51**, 613; Jahr. Chem. 1880, **33**, 1005. Monatsh. Chem. 1905, **26**, 1420. J. C. S. 1891, **60**, 165; Chem. Centr. 1888, **59**, 1060; J. C. S. 1889, **56**, 116. K. Zuhlkowsky and B. Franz, Ber. oesterr. Ges. zur Foerderung d. chem. Ind. 1894, **16**, 120.
10. J. S. C. I. 1909, **28**, 288; abst. Zts. ang. Chem. 1909, **22**, 2346; Bull. Soc. Chim. 1909, (4), **6**, 1152; Chem. Zentr. 1909, **80**, I, 1989; Jahr. Chem. 1909, **62**, 378. For reactions of starch with acetic anhydride, see P. Schützenberger, Ann. Chim. Phys. 1870, (4), **21**, 235; abst. Chem. Centr. 1871, **42**, 568; Ann. 1871, **160**, 74; J. C. S. 1872, **25**, 356; abst. Chem. Centr. 1871, **42**, 740.
11. C. Cross, E. Bevan and J. Briggs, Jour. Soc. Dyers Col. 1907, **23**, 250. C. Cross, E. Bevan and J. Traquair, Chem. Ztg. 1905, **29**, 527; Wag. Jahr. 1905, **51**, II, 197; Chem. Centr. 1905, **76**, II, 36.
12. J. Russ. Phys. Chem. Soc. 1905, **37**, 421; abst. Brewers Jour. 1905, **41**, 688; J. S. C. I. 1905, **24**, 1246; Jahr. Chem. 1905–1908, II, 954; Chem. Centr. 1905, **76**, II, 1029; J. C. S. 1904, **86**, i, 798. Compare also Z. Skraup, E. Geinsperger, E. v. Knaffl-Lenz, F. Menter and H. Sirk, Monatsh. 1905, **26**, 1415; abst. J. C. S. 1906, **90**, i, 67; J. S. C. I. 1906, **25**, 43; Bull. Soc. Chim. 1906, **36**, 591; Chem. Centr. 1906, **77**, II, 655; Jahr. Chem. 1905-1908, II, 929. J. Boeseken, J. van den Berg and A. Kerstjens (Rec. trav. chim. Pays-Bas, 1916, **35**, 320; abst. J. C. S. 1916, **109**, i, 308; C. A. 1917, **11**, 39) have found that the velocity of acetylation of starch is less than that of cellulose, hydriodic acid being the best catalyst. In the case of sulfuric acid, an increase in the amount of acid used produces an acceleration in esterification, but not to an extent proportional to the amount of catalyst employed.
13. Bull. Acad. Roy. Belg. 1911, 213, 335; abst. J. C. S. 1911, **100**, 423; Chem. Zentr. 1911, **82**, II, 855; C. A. 1911, **5**, 2443. For the hydrolyzing

described in detail in Volume VIII of this series already published.

As the result of the researches of C. Cross and J. Traquair on the partial acetylation of starch,[1] certain patents have been issued to them[2] and W. Wotherspoon[3] for the manufacture of a starch acetate intended for textile purposes and known under the commercial name of "Feculose," for which many technical uses have been pointed out by the inventors[4] and by F. Farrell.[5] A. Militz[6] and F. Bayer & Co.,[7] together with W. Dixon,[8] have also investigated the technical side of these products.

The benzoylation of starch in the hands of C. Cross,[9] E.

---

action of formic acid on starch, see W. Oechsner de Conick, Bull. Acad Roy. Belg. 1910, 515, 586; abst. C. A. 1911, **5**, 394; J. C. S. 1910, **98**, 654; Chem. Zentr. 1910, **81**, II, 1459. See also L. Schulze, J. prakt. Chem. 1883, **136**, 324; I. Frankhausen, Dingl. Poly. 1887, **266**, 303. For the preparation of soluble starch by heating with dilute acetic acid, see E. Blumer, D. R. P. 137330, 1901; abst. Chem. Centr. 1901, **72**, I, 306; Jahr. Chem. 1903, **56**, 1005; Zts. ang. Chem. 1903, **16**, 90. F. P. 322206, 1902; abst. J. S. C. I. 1903, **22**, 310. E. P. 10872, 1902. Aust. P. 14886, 1904. Farbenfabriken vorm. F. Bayer & Co., D. R. P. 200145; abst. Jahr. Chem. 1905–1908, II, 941.

1. C. Cross, E. Bevan and J. Traquair, Chem. Ztg. 1905, **29**, 527; abst. J. C. S. 1905, **88**, i, 511. J. Traquair, J. S. C. I. 1909, **28**, 288; abst. Zts. ang. Chem. 1909, **22**, 2346; Bull. Soc. Chim. 1909, (4), **6**, 1053; C. A. 1909, **3**, 2070. J. S. C. I. 1910, **29**, 323; abst. Bull. Soc. Chim. 1910, (4), **8**, 1150. See also J. Traquair, J. S. C. I. 1910, **29**, 323; 1912, **31**, 1016.

2. E. P. 9868, 1902; abst. J. S. C. I. 1903, **22**, 1008; Mon. Sci. 1904, **60**, 37. U. S. P. 778173, 1904; abst. J. S. C. I. 1905, **24**, 98. See also J. Traquair, J. S. C. I. 1909, **28**, 288; 1910, **29**, 323; 1912, **31**, 1016.

3. F. P. 334154, 1903; abst. J. S. C. I. 1904, **23**, 29. D. R. P. 182558, 1903; abst. Zts. ang. Chem. 1907, **20**, 1781; Mon. Sci. 1909, **70**, 77. Belg. P. 171743, 1903. Aust. P. 27352, 1907. For additional commercial applications of the starch acetates, refer to F. Bayer & Co., D. R. P. 200145. Swiss P. 39840, 1907. Aust. P. 37386, 1909. J. Boeseken, J. v. den Berg and A. Kerstjens, Rec. trav. chim. 1916, **35**, 320; abst. J. C. S. 1916, **109**, i, 308. Staier, U. S. P. 1144073; abst. C. A. 1915, **9**, 2313. A. Strut ers, E. P. 27479, 1912. H. Wheelwright, U. S. P. 1195888, 1916; abst. J. S. C. I. 1916, **35**, 1009.

4. J. S. C. I. 1909, **28**, 288; abst. Zts. ang. Chem. 1909, **22**, 2346; Bull. Soc. Chim. 1909, (4), **6**, 1152. J. S. C. I. 1910, **29**, 323; abst. Zts. ang. Chem. 1910, **23**, 1824; Bull. Soc. Chim. 1910, (4), **8**, 1151. Pharm. Jour. No. 2379, 680; abst. Merck's Rep. 1909, **18**, 179; Mon. Sci. 1910, **72**, 605.

5. J. Soc. Dyers Col. 1908, **24**, 323; abst. Zts. ang. Chem. 1909, **22**, 221; J. S. C. I. 1909, **28**, 19.

6. U. S. P. 941159, 1909; abst. J. S. C. I. 1909, **28**, 1322; C. A. 1910, **4**, 525.

7. E. P. 25274, 1907; abst. J. S. C. I. 1908, **27**, 761. F. P. 383902, 1907; abst. J. S. C. I. 1908, **27**, 415. D. R. P. 200145, 214244, 1909. Aust. P. 37386, 1909. Swiss P. 39840, 1907.

8. E. P. 27491, 1911; abst. J. S. C. I. 1913, **32**, 214; C. A. 1913, **7**, 1789.

9. C. Cross and E. Bevan, J. C. S. 1893, **26**, 837; Chem. News, 1890, **61**, 87. C. Cross, E. Bevan and R. Jenks, Ber. 1901, **34**, 2496. C. Cross and E. Bevan, Ber. 1901, **34**, 1514; J. C. S. 1901, **80**, i, 452; Chem. Centr. 1901, **72**, II, 94; Jahr. Chem. 1901, **54**, 891.

Baumann,[1] O. Hauser and H. Muschner,[2] and of H. Ost and F. Klein[3] have thrown considerable light upon some angles of carbohydrate chemistry, but the starch benzoates have, as yet, acquired no technical significance.

Starch forms compounds with tannic acid.[4]

Action of Enzymes on Starch. The action of saliva upon different kinds of starch has been investigated by Lefberg and Georgieski,[5] who found that potato starch is converted into sugar more easily than wheat starch, while corn starch occupies an intermediate place. Soluble starch was found to behave the same as potato starch.

Ptyalin also converts starch into sugar in the presence of impure gastric juice,[6] but the action is suspended in pure gastric juice, to again become active in the duodenum. Diastase is completely deprived of its power of converting starch to sugar by HCl or pure gastric juice. According to E. Bourquelot,[7] when starch has been heated with water at a definite temperature and then cooled down to the ordinary temperature, the saliva acts only on that portion of the starch which has undergone hydration. He found that the hydrating action of water begins at about 35°, increase somewhat irregularly up to 74°, beyond which an increase of temperature exerts no appreciable effect.

W. Biedermann has shown[8] that dilute, boiled starch solution can be hydrolyzed with comparative rapidity by saliva, but that upon boiling the latter, hydrolysis takes place only after a

---

1. E. Baumann. Ber. 1886, **19**, 3218; abst. J. C. S. 1887, **52**, 228; Jahr. Chem. 1886, **39**, 1426.

2. Zts. ang. Chem. 1913, **26**, 137; J. S. C. I. 1913, **32**, 357; Chem. Zentr. 1913, **84**, I, 1412; J. Dyers and Col. 1913, **29**, 194; Kunst. 1913, **3**, 330; C. A. 1913, **7**, 2854; J. C. S. 1913, **104**, i, 363.

3. Zts. ang. Chem. 1913, **26**, 437; J. S. C. I. 1913, **32**, 823; Kunst. 1913, **3**, 331; C. A. 1913, **7**, 3661; J. C. S. 1913, **104**, i, 1043; Chem. Zentr. 1913, **85**, II, 1293.

4. J. v. Kalinowsky, J. prakt. Chem. 1845, **35**, 201.

5. J. Russ. Phys. Chem. Soc. 1876, No. 1; abst. J. C. S. 1876, **30**, 398; Bull. Soc. Chim. 1876, **25**, 393.

6. T. Defresne, Compt. rend. 1879, **89**, 1070; abst. Chem. News, 1880, **41**, 22; J. C. S. 1880, **38**, 330; J. pharm. chim. 1880, (5), **1**, 168; Jahr. Chem. 1879, **32**, 1019.

7. Compt. rend. 1887, **104**, 71, 177; abst. Chem. News, 1887, **55**, 81, 94; J. C. S. 1887, **52**, 354, 355; Ber. 1887, **20**, R, 109, 143; Jahr. Chem. 1887, **40**, 2265, 2319. J. pharm. chim. 1891, (5), **24**, 197; abst. J. C. S. 1892, **62**, 230.

8. Fermentforschung, 1916, **1**, 474; abst. C. A. 1917, **11**, 1436; J. C. S. 1917, **112**, i, 62; J. S. C. I. 1917, **36**, 230; Chem. Zentr. 1916, **87**, II, 496.

much longer period of contact. As pointed out by C. Gessard[1] and I. Wolff,[2] serums can be prepared which inhibit the action of malt extract upon starch, the maximum inhibition being 70%, as determined by the amount of maltose produced. At 50° the inhibitory effect is but half that at 20°. M. Bial[3] and F. Roehmann[4] have shown that human blood serum and lymph serum contain an enzyme capable of converting starch into dextrin, maltose and glucose.[5]

Lepetit, Dollfuss & Gansser[6] convert starch into partially or completely soluble products by means of pancreas or pancreatic extract.

A. Dobroslavine,[7] M. Maercker,[8] W. Watson,[9] F. Musculus and J. de Mering,[10] A. Lea,[11] E. Bourquelot,[12] have shown that, in

[1] C. Gessard, Compt. rend. 1906, **142**, 641; Compt. rend. Soc. Biol. 1906, **61**, 425; abst. J. C. S. 1906, **90**, ii, 373.

[2] C. Gessard and J. Wolff, Compt. rend. 1908, **146**, 414; abst. J. C. S. 1908, **94**, i, 379.

[3] Pflueger's Archiv. 1892, **52**, 137; 1893, **53**, 157; **54**, 72; abst. J. C. S. 1893, **64**, ii, 333, 581; Ber. 1892, **25**, R, 647, 912; 1893, **26**, R, 412; Chem. Centr. 1892, **63**, II, 82, 1021; Jahr. Chem. 1892, **45**, 2369; 1893, **46**, 1999.

[4] Ber. 1892, **25**, 3654; Pflueger's Archiv. 1893, **53**, 157; abst. J. C. S. 1893, **64**, i, 187; ii, 333; 1895, **68**, ii, 52; J. S. C. I. 1893, **12**, 336; Bull. Soc. Chim. 1893, **10**, 413; 1895, **14**, 694; Ber. 1892, **25**, R, 647; 1894, **27**, 3251; Chem. Centr. 1893, **64**, I, 350; Jahr. Chem. 1892, **45**, 2363, 2466; 1894, **47**, 2332.

[5] The author finds that 100 gm. of potato starch when mixed with 5 liters of water, and after cooling, 1 liter of bullock's blood serum and 100 cc. of 10% alcoholic solution of thymol added, that after 24 hours at 32°, glucose and acroodextrin are the chief products formed. He claims erythrodextrin is not a mixture of starch and acroodextrin, as stated by A. Schifferer, N. Zts. Rüb. Zucker. Ind. 1892, **29**, 167; abst. J. S. C. I. 1893, **12**, 368.

[6] F. P. 466275, 466276, 1913; abst. C. A. 1915, **9**, 724; J. S. C. I. 1914, **33**, 590. D. R. P. 285050, 1913; abst. C. A. 1916, **10**, 254; Chem. Zentr. 1915, **86**, I, 211; Chem. Ztg. Rep. 1915, **39**, 263; Zts. ang. Chem. 1915, **28**, II, 402. See O. Nasse, Pflueger's Archiv. 1877, **14**, 473; **15**, 471; abst. J. C. S. 1877, **32**, 503; Jahr. Chem. 1878, **31**, 1034.

[7] Bull. Soc. Chim. 1876, **26**, 452; J. Russ. Phys. Chem. Soc. 1876, **8**, I, 57; abst. J. C. S. 1877, **31**, 453.

[8] Landwirthschaftliche Versuchs-Stationen **23**, 69; Münch. Naturforscher Vers. 1877, 222; abst. J. C. S. 1878, **34**, 969; Ber. 1877, **10**, 2234; Chem. Centr. 1878, **49**, 559; Jahr. Chem. 1877, **30**, 900; 1878, **31**, 1035. For the action of enzymes upon starches of different origin, see H. Sherman, F. Walker and M. Caldwell, J. A. C. S. 1919, **41**, 1123; abst. C. A. 1919, **13**, 2297.

[9] J. C. S. 1879, **35**, 539; Pharm. J. Trans. (3), **9**, 987; Chem. News, 1879, **39**, 226; abst. Ber. 1879, **12**, 1217; Jahr. Chem. 1879, **32**, 958.

[10] Zts. physiol. Chem. 1877, **1**, 395; 1878, **2**, 420; abst. Jahr. Chem. 1877, **30**, 1024; 1878, **31**, 994. Compt. rend. 1879, **88**, 87; abst. Bull. Soc. Chim. 1879, **31**, 105; Chem. News, 1879, **39**, 64; J. C. S. 1879, **36**, 370; Ber. 1879, **12**, 379, 672, 700; Jahr. Chem. 1879, **32**, 1077.

[11] J. Physiol. 1890, **11**, 226; Proc. Roy. Soc. 1890, **47**, 192; abst. J. C.

general, the products of enzymatic action on starch are maltose, a reducing, unfermentable dextrin, and a small amount of dextrose. Ungelatinized starch is unacted upon by ptyalin, but at a temperature slightly below the gelatinizing point the starch is dissolved, the action being most pronounced when the ferment is allowed to act upon the starch at a temperature of 60°.

Enzymes capable of dissolving starch have not only been observed in the pancreatic juice,[1] but in the small intestine, liver,[2] and in many other animal tissues,[3] including those of blood[4] and of fish.[5] Of the bacteria, the *Bacillus macerans*,[6] *Mucor boulard*,[7] *Bacterium burdigalenes*[8] *Bacillus butyricus*,[9] *Bacillus amylobacter*,

---

S. 1890, **58**, 536; Chem. Centr. 1890, **61**, I, 1069; Jahr. Chem. 1890, **43**, 2266.

[12] Compt. rend. 1886, **104**, 71, 177; abst. Chem. News, 1887, **55**, 81, 94; J. C. S. 1887, **52**, 354, 355; Ber. 1887, **20**, R, 109, 143; Jahr. Chem. 1887, **40**, 2265, 2319.

[1] H. Brown and J. Heron, J. C. S. 1879, **35**, 596; Zts. Chem. Grossgewerbe, 1879, **6**, 153, 254, 259; Chem. News, 1879, **39**, 284; 1880, **41**, 22; **42**, 63; 1881, **43**, 154; Ann. 1879, **199**, 165; Ber. 1879, **12**, 1477; Chem. Tech. Rep. 1879, **8**, II, 163; Jahr. rein Chem. 1879, **7**, 507; Jahr. Chem. 1879, **32**, 838; Zts. ges. Brauw. **14**, 442.

[2] Wittich, Pflügers Arch. f. Physiol. 1872, **6**, 181; 1873, **7**, 28; abst. J. C. S. 1872, **25**, 1105; 1873, **26**, 515; Bull. Soc. Chim. 1873, **20**, 414. C. Bernard, Compt. rend. 1877, **85**, 519; abst. J. C. S. 1878, **34**, 82; Bull. Soc. Chim. 1879, **31**, 136; Jahr. Chem. 1877, **30**, 980. M. Abeles, Jahr. Thier. 1876, **6**, 271; Medizin. Jahrbücher, 1876, 225.

[3] W. Ellenberger and V. Hofmeister, Jahr. Thier. 1882, **12**, 501; Archiv. wiss. Prakt. Thierheilkunde, 1882, **8**, 91; abst. J. C. S. 1882, **42**, 1119. V. Paschutin, Jahr. Thier. 1871, **1**, 304. Centr. med. wiss. 1870, 561, 577; 1872, 97; Archiv. Anat. Physiol, 1871, 305; 1873, 382; abst. J. C. S. 1873, **26**, 1064; Bull. Soc. Chim. 1873, **20**, 310; Jahr. Chem. 1870, **23**, 907; 1872, **25**, 934; 1874, **27**, 1057; Zts. anal. Chem. 1872, **11**, 464; 1874, **13**, 104.

[4] E. Bimmerman, Pflügers Arch. f. Physiol. 1879, **20**, 201; abst. J. C. S. 1880, **38**, 677; Ber. 1879, **12**, 2168; Jahr. Chem. 1879, **32**, 959. P. Plosz, and E. Tiegel, Pflügers Arch. f. Physiol. 1873, **7**, 391; abst. J. C. S. 1873, **26**, 1245.

[5] C. Ricket, Jahr. Thier. 1884, **14**, 359. C. Kruckenberg, Unter. Phys. Inst. Heidelberg, **1**, 2.

[6] H. Pringsheim and F. Eissler, Ber. 1913, **46**, 2959; 1914, **47**, 256; abst. J. C. S. 1913, **104**, i, 1156; 1915, **108**, i, 108, 382; J. S. C. I. 1913, **32**, 985; C. A. 1914, **8**, 118; 1915, **9**, 83. See also E. Moreau, Ann. Falsif. 1911, **4**, 65; abst. J. S. C. I. 1911, **30**, 439. H. Pringsheim and A. Langhans, Ber. 1912, **45**, 2533; abst. J. C. S. 1912, **102**, i, 832; J. S. C. I. 1912, **31**, 1001. F. Schardinger, Zentr. Bakt. Parasitenk. **14**, ii, 772; **19**, 161; 1908, **22**, ii, 98; 1911, **29**, 188; abst. J. C. S. 1911, **100**, i, 181; J. S. C. I. 1909, **28**, 153; 1911, **30**, 439; Chem. Zentr. 1908, **79**, I, 68; 1911, **82**, I, 874.

[7] Soc. d'Exploit des Proc. H. Boulard, E. P. 25406, 1913; abst. J. S. C. I. 1914, **33**, 659; C. A. 1915, **9**, 1223. F. P. 464601, 1913, 477927, 1914; abst. J. S. C. I. 1914, **33**, 497; 1916, **35**, 1170.

[8] H. Joucla, F. P. 474948, 1914; 478972, 1915; abst. J. S. C. I. 1915, **34**, 1107; 1916, **35**, 1172; C. A. 1916, **10**, 2274.

[9] A. Villiers, Compt. rend. 1891, **112**, 435, 536; 1891, **113**, 144; abst. J. C. S. 1891, **60**, 1446; J. S. C. I. 1891, **10**, 474, 717; Chem. News, 1891, **63**, 284; **64**, 74; Bull. Soc. Chim. 1891, **5**, 468, 470, 546; Ber. 1891, **24**, R, 272, 319, 734; Jahr. Chem. 1891, **44**, 2336.

Bacillus suaveolens[1] and *Bacillus amylozymicus*[2] all possess this property when in contact with starch under favorable conditions.

Certain organisms, bacteria, enzymes and moulds are apparently able to secrete a product having the power of dissolving starch, as indicated by the researches of A. Fitz,[3] A. Aulard,[4] S. Benni,[5] J. Kjeldahl,[6] V. Marcano,[7] J. Sanguinetti,[8] A. Sclavo and B. Gosio,[9] and G. Bouchardat.[10] The latter by the hydrolysis of starch obtained ethyl, propyl and butyl alcohols and acetates. In general, the nature of the dissolution products has been but imperfectly studied. According to J. Wortman,[11] A. Fitz,[12] V. Marcano,[13] U. Gayon and E. Dubourg,[14] R. Atkinson[15]

---

[1] F. Selivanoff, J. Russ. Phys. Chem. Soc. 1889, **21**, 27; abst. J. C. S. 1889, **56**, 1132.

[2] J. Wortmann, Zts. Physiol. Chem. **6**, 287; abst. J. C. S. 1883, **40**, 930; Mon. Sci. 1883, **25**, 45; Ber. 1882, **15**, 2269; Jahr. Chem. 1882, **35**, 1247. Bot. Ztg. 1890, **48**, 582, 597, 617, 633, 657; abst. J. C. S. 1891, **60**, 856; Chem. Centr. 1890, **61**, II, 821; Dingl. Poly. 1892, **283**, **284**; Jahr. Chem. 1892, **45**, 2823. See also A. Stutzer and A. Isbert, Zts. physiol. Chem. 1887, **12**, 73; abst. J. C. S. 1888, **54**, 170; Ber. 1888, **21**, R, 541; Chem. Centr. 1887, **58**, 1551; Jahr. Chem. 1887, **40**, 2322.

[3] Ber. 1876, **9**, 1348; 1877, **10**, 276, 2226; abst. J. C. S. 1877, **31**, 226; Chem. News, 1877, **35**, 105; 1878, **37**, 161; Bull. Soc. Chim. 1876, **26**, 473; 1877, **28**, 24; 1878, **29**, 472; Chem. Tech. Rep. 1876, **15**, I, 128, 130; Jahr. Chem. 1875, **28**, 885; 1876, **29**, 343, 950.

[4] Proc. Seventh Inter. Cong. Appl. Chem. 1909, Sect. VI-B; abst. J. S. C. I. 1911, **30**, 234; C. A. 1911, **5**, 1969.

[5] Russ. P. 1198, 1898; abst. Zts. Spiritusind. 1900, **23**, 276; J. S. C. I. 1900, **19**, 836; Mon. Sci. 1899, **54**, 145; Chem. Centr. 1899, **70**, I, 784; Chem. Tech. Rep. 1899, **38**, 481; Chem. Ztg. 1899, **23**, 203; Jahr. Chem. 1899, **52**, 1272.

[6] Resume du Compt. rend. des Travaux du Laboratoire de Carlsberg, 1879; abst. Zts. ges. Brauwesen, 1880, 49; Dingl. Poly. 1880, **235**, 379; J. C. S. 1880, **38**, 562; 1881, **40**, 115; Bied. Centr. 1880, **9**, 689; Chem. Centr. 1880, **51**, 73; Jahr. Chem. 1880, **33**, 1122; Wag. Jahr. 1880, **26**, 624.

[7] Compt. rend. 1882, **95**, 345, 856; abst. J. C. S. 1882, **42**, 1311; Chem. News, 1882, **46**, 122, 254; J. pharm. chim. 1882, (5), **7**, 168; Ber. 1882, **15**, 3089; Chem. Tech. Rep. 1883, **22**, II, 44; Jahr. Chem. 1882, **35**, 1236; Wag. Jahr. 1882, **28**, 800.

[8] Ann. Inst. Pasteur, 1897, **11**, 264; abst. La Biere, **5**, 49; J. S. C. I. 1897, **16**, 626; Chem. Centr. 1897, **68**, I, 998.

[9] Bied. Centr. 1891, **20**, 419; abst. J. C. S. 1891, **60**, 1284; Arch. Ital. Biol. **14**; Staz. sperim. agrar. ital. **19**, 540; Jahr. Chem. 1890, **43**, 2303.

[10] Compt. rend. 1874, **78**, 1145; abst. J. C. S. 1874, **27**, 883; Mon. Sci. 1874, **16**, 553; Ber. 1874, **7**, 657, 746; Chem. Tech. Rep. 1874, **13**, I, 51; Jahr. Chem. 1874, **27**, 950; Wag. Jahr. 1874, **20**, 661. See also E. P. 768, 1858.

[11] Zts. Physiol. Chem. **6**, 287; abst. J. C. S. 1883, **40**, 930; Mon. Sci. 1883, **25**, 45; Ber. 1882, **15**, 2269; Jahr. Chem. 1882, **35**, 1247.

[12] Ber. 1876, **9**, 1348; 1877, **10**, 276, 2226; abst. Chem. News, 1877, **35**, 105; 1878, **37**, 161; Bull. Soc. Chim. 1876, **26**, 473; 1877, **28**, 24; **29**, 472; Chem. Tech. Rep. 1876, **15**, I, 128, 130; Jahr. Chem. 1875, **28**, 885; 1876, **29**, 343, 950.

[13] Compt. rend. 1882, **95**, 345, 856; J. pharm. chim. 1882, (5), **7**, 168;

and J. Takamine,[1] investigations have not conclusively gone beyond the statement that sugar, sugars and dextrin are among the products of transformation. It would appear that some gums of the arabin and bassorin group contain a starch-splitting enzyme.[2]

It has long been known that corn, either malted or raw, as well as some other grains, contains an enzyme capable of dissolving starch to produce glucose as a final product.[3] Its action upon starch is not as vigorous as on dextrose, while maltose is rapidly converted into dextrose.[4]

As yet, no exhaustive work has appeared as to the differences in action between moulds and enzymes upon carbohydrates.

Formaldehyde and Starch. F. Beltzer[5] has given a summary

---

abst. Chem. News, 1882, **46**, 122, 254; J. C. S. 1882, **42**, 1311; Ber. 1882, **15**, 3089; Chem. Tech. Rep. 1883, **22**, II, 44; Jahr. Chem. 1882, **35**, 1236; Wag. Jahr. 1882, **28**, 800.

[14] Compt. rend. 1886, **103**, 885; abst. Chem. News, 1886, **54**, 273; J. C. S. 1887, **52**, 171; J. S. C. I. 1887, **6**, 144; Bull. Soc. Chim. 1887, **47**, 649; J. pharm. chim. 1886, (5), **14**, 567; Mon. Sci. 1886, **28**, 1441; Ber. 1887, **20**, R, 13; Chem. Tech. Rep. 1886, **25**, II, 87; Chem. Ztg. Rep. 1886, **10**, 259; Der Bierbrauer, 1886, 566; Industriebl. 1887, 118; Jahr. Chem. 1886, **39**, 1884.

[15] Proc. Roy. Soc. 1881, **31**, 523; **32**, 299; Chem. News, 1880, **41**, 169; abst. J. C. S. 1881, **40**, 1059; J. pharm. chim. 1882, (5), **5**, 157; Mon. Sci. 1882, **24**, 7; Ber. 1881, **14**, 2287; Chem. Centr. 1880, **51**, 278; Chem. Tech. Rep. 1880, **19**, I, 90; Jahr. Chem. 1880, **33**, 1134; 1881, **34**, 985; Wag. Jahr. 1880, **26**, 629.

[1] E. P. 5700, 17374, 1891; abst. J. S. C. I. 1891, **10**, 1019; 1892, **11**, 1022. F. P. 214033, 216840, 1891; abst. Mon. Sci. 1892, **40**, 91, 266; 1894, **44**, 591. D. R. P. 79763; abst. Ber. 1895, **28**, R, 578; Chem. Centr. 1895, **66**, I, 1128; Chem. Tech. Rep. 1895, **34**, I, 92; Wag. Jahr. 1895, **41**, 908. D. R. P. 84588; abst. Ber. 1896, **29**, 194; Chem. Tech. Rep. 1896, **35**, 60; Chem. Ztg. 1896, **20**, 156; Wag. Jahr. 1896, **42**, 907. See also Chem. News, 1898, **77**, 137; 1901, **84**, 23. Jahr. Chem. 1891, **44**, 2745; 1895, **48**, 2696; Meyer Jahr. Chem. 1894, **4**, 450; 1896, **6**, 363; 1897, **7**, 352. U. S. P. 562103, 1896.

[2] O'Sullivan, J. C. S. 1891, **59**, 1061; abst. J. S. C. I. 1892, **11**, 48; Ber. 1892, **25**, R, 370; Jahr. Chem. 1891, **44**, 2212; Chem. Centr. 1892, **63**, I, 137.

[3] L. Cuisinier, D. R. P. 37923, 1884. E. P. 1820, 1886. F. P. 171958, 1885; abst. J. C. S. 1887, **52**, 354; J. S. C. I. 1887, **6**, 375; Mon. Sci. 1886, **28**, 718, 840; Ber. 1887, **20**, 128; Chem. Centr. 1886, **57**, 614; Chem. Tech. Rep. 1884, **23**, II, 118; 1887, **26**, I, 77, 172; II, 194; Jahr. Chem. 1886, **39**, 1782, 2143, 2144; 1887, **40**, 2660; Wag. Jahr. 1886, **32**, 611.

[4] R. Geduld, Wochenschrift f. Brauerei, 1891, **8**, 620; abst. J. S. C. I. 1892, **11**, 627; Chem. Centr. 1891, **62**, II, 323; Dingl. Poly. 1892, **285**, 184, 211; Jahr. Chem. 1892, **45**, 2823. C. Lintner, Zts. f. ges. Brau. 1892, **15**, 123; abst. J. C. S. 1893, **64**, i, 4; J. S. C. I. 1892, **11**, 1021; Chem. Centr. 1892, **63**, I, 740; Jahr. Chem. 1892, **45**, 2466; Wag. Jahr. 1892, **38**, 878.

[5] Eighth Intl. Cong. Appl. Chem. 1912, **7**, 7; abst. C. A. 1912, **6**, 3185; 1913, **7**, 551; J. S. C. I. 1912, **31**, 868; Kunst. 1912, **2**, 442; Wag. Jahr. 1912, **58**, II, 445; Zts. ang. Chem. 1913, **26**, II, 303.

of the action of formaldehyde upon starches. In the process of E. Blumer,[1] a mixture of dilute alkali hydroxide (5° Bé.) and formaldehyde is allowed to act upon starch for some hours, when it is heated for a short time, and the product then washed with water until no odor of formalin can be detected, then with dilute acetic acid, and finally dried carefully at a low temperature (not over 50°).

In the method of A. Classen,[2] formalin and starch are mixed and heated in a closed vessel to 100°–120° for 5–6 hours, after which the product is removed and treated as above indicated. It finds a use therapeutically as a topical application to wounds on account of the antiseptic action due to the constant liberation of formaldehyde.[3]

According to H. Maggi and G. Woker,[4] the dialysate from a mixture of starch and formaldehyde has properties of a solution of dextrin and the simpler carbohydrates. A precipitate produced by the addition of alcohol to such a dialysate re-dissolves in water, and slowly reverts to dextrin upon standing. Woker[5] has also shown that diastase can behave as a peroxydase or catalase, and that solutions of starch and glycogen suffer hydrolysis when exposed to relatively large amounts of formaldehyde,

---

[1] D. R. P. 179590, 1904; abst. J. S. C. I. 1907, **26**, 1066; Chem. Zentr. 1907, **78**, I, 383; Chem. Ztg. Rep. 1907, **31**, 27; Jahr. Chem. 1905–1908, II, 948; Wag. Jahr. 1906, **52**, II, 79; Zts. ang. Chem. 1907, **20**, 1246; Friedlaender, **8**, 917.

[2] A. Classen, D. R. P. 92259, 1896; abst. Chem. Centr. 1897, **68**, II, 456; Chem. Ztg. 1897, **21**, 539; Jahr. Chem. 1897, **50**, 1516; 1898, **51**, 1242; Wag. Jahr. 1897, **43**, 623. D. R. P. 94628, 1896; abst. Chem. Centr. 1898, **69**, I, 295; Chem. Ztg. 1897, **21**, 1004. D. R. P. 99378, 1899; abst. Chem. Centr. 1899, **70**, I, 160; Chem. Ztg. 1898, **22**, 963; Jahr. Chem. 1898, **51**, 124; Wag. Jahr. 1898, **44**, 559.

[3] D. R. P. 94282, 1896; abst. Chem. Centr. 1898, **69**, I, 229; Chem. Ztg. 1897, **21**, 963; Jahr. Chem. 1897, **50**, 1645; Wag. Jahr. 1897, **43**, 623; Friedlaender, **6**, 1129. E. P. 1144, 1897; abst. J. S. C. I. 1897, **16**, 459. The combination of formaldehyde with starch has been called "amyloform," while that with dextrin has been named "dextroform." For additional data on amyloform and glutols, see A. Classen, Therap. Monatsh. 1897, **11**, 33; Muench. med. Wochschr. **44**, 307; abst. Chem. Centr. 1897, **78**, I, 395, 939. C. Schleich, Therap. Monatsh. 1897, **11**, 97; abst. Chem. Centr. 1897, **78**, I, 715. A. Gottstein, Therap. Monatsh. 1897, **11**, 95; abst. Chem. Centr. 1897, **78**, I, 715.

[4] Ber. 1918, **51**, 790; abst. J. C. S. 1918, **114**, i, 375; C. A. 1918, **12**, 700. Cf. G. Woker, J. S. C. I. 1916, **35**, 1268. M. Jacoby, Ber. 1919, **52**, 558; abst. J. S. C. I. 1919, **38**, 508-A. W. v. Kaufmann and A. Lewite, Ber. 1919, **52**, 616; abst. J. S. C. I. 1919, **38**, 508-A. W. Biedermann, Fermentforsch. 1916, **1**, 474. J. Wohlgemuth, Biochem. Zts. 1919, **94**, 213.

[5] Ber. 1916, **49**, 2311; abst. J. C. S. 1917, **112**, i, 61, 62, 447, 485; C. A. 1917, **11**, 2090, 3259.

although the aldehyde is more pronounced as a prototype of a peroxydase than of diastase. Although formalin is a powerful enzymatic toxic, a 2–5% solution of it appears to accelerate the action of diastase.[1]

According to V. Syniewsky,[2] when potato starch is left for two months in the presence of 40% solution of formaldehyde, a mobile, opalescent fluid results which must be regarded as a definite compound, but, however, has not been isolated in the pure state, due to the fact that upon evaporation and heating, formaldehyde is volatilized. If this solution is diluted with water formaldehyde gradually separates and the iodine reaction of the solution passes from brown to blue. Inasmuch as the product remaining in solution when the blue reaction has been reached can be precipitated by alcohol, it would appear to be a product of the hydrolysis of starch.

Starch and Heat. When in an entirely anhydrous condition, starch may be heated to a temperature of 155°–160° without undergoing any apparent change. At higher temperatures it becomes dextrinated and darkens in color. However, when ordinary air-dried starch is heated to 150°–160° it readily decomposes, giving rise to a number of products, of which dextrin and reducing sugars predominate. The action varies within comparatively wide limits, depending upon the kind and purity of the starch heated. In the E. Nowak process[3] the starch is rendered slightly alkaline before being subjected to the heat treatment.

S. Schubert has recorded[4] that a microscopic examination of starch granules at 160° shows the presence of gas bubbles, which increase when the temperature is raised to 175°; that this alteration of the starch granule by heat converts the granulose into soluble starch and dextrin, while the cellulosic layers are only

---

[1] Zts. ges. Brauw. 1908, **31**, 161; abst. J. C. S. 1908, **94**, i, 606; Chem. Zentr. 1908, **79**, i, 1834; C. A. 1908, **2**, 2881; J. S. C. I. 1908, **27**, 461; Jahr. Chem. 1905–1908, II, 948; Meyer Jahr. Chem. 1908, **18**, 392; Wag. Jahr. 1908, **54**, II, 191.

[2] Ann. 1902, **324**, 201; abst. J. C. S. 1903, **84**, i, 68; Bull. Acad. Sci. Cracow, 1902, 435; J. S. C. I. 1902, **21**, 1341; Chem. Centr. 1902, **73**, II, 986, 1248; Jahr. Chem. 1902, **55**, 1039.

[3] E. P. 22542, 1903; abst. J. S. C. I. 1904, **23**, 32; Chem. Ztg. 1905, **29**, 203.

[4] Ber. 1884, **17**, 479; Monatsh. 1884, **5**, 472; abst. J. C. S. 1885, **48**, 368. Oesterr-ung. Zts. Zucker. Ind. Landw. 1910, **39**, 411; abst. Chem. Zentr. 1910, **81**, II, 688; J. C. S. 1911, **100**, ii, 75.

attacked at higher temperatures. When starch which has been subjected to a high temperature is treated with water, the soluble starch, dextrin and other products of decomposition are dissolved, while the insoluble matter that is left, is an organized residuum having the structure of the original granule, and soluble in hot water.

In experiments to ascertain the temperature at which starch suffers the maximum loss in weight without decomposition, F. Dafert[1] found that at 120° the loss was 11.31%; 105°–117°, 10.89%; 100° in vacuum, 11.9%; in but the first case was the starch changed, and then only slightly. When starch and cellulose are heated[2] gradually under a pressure of 12–15 mm., the fraction distilling between 200°–300° amounts to about 45% of the original, and consists of an oily crystalline mass, from which crystals have been separated corresponding to the laevoglucosan of C. Tanret.[3] By dry distillation at atmospheric pressure, starch yields water, carbon dioxide, gaseous hydrocarbons, acetic and homologous acids, and empyreumatic oil, and leaves a porous charcoal.

It has been shown[4,5] that by heating purified starch or cellulose in an atmosphere of pure and dry hydrogen, as much as 95% of methane can be obtained. This when chlorinated to methyl chloride, the latter hydrolyzed to methyl alcohol, and this partially oxidized, produces formaldehyde—a sort of reversible synthesis. O. Loew[6] has observed that formalin and lime water

---

[1] Landw. Jahr. 1885, 837; 1886, 259; Ber. bot. Ges. 1887, 108; Bied. Centr. 1886, **15**, 133; Chem. Centr. 1887, **58**, 567; abst. J. C. S. 1886, **50**, 527; 1887, **52**, 1143.

[2] Compt. rend. 1918, **166**, 38; abst. J. C. S. 1918, **114**, i, 59; J. S. C. I. 1918, **37**, 49-A; C. A. 1918, **12**, 804, 2187.

[3] Compt. rend. 1894, **119**, 158; abst. J. C. S. 1894, **66**, i, 564; Chem. Centr. 1894, **65**, II, 360; Jahr. Chem. 1894, **47**, 112; Chem. Ztg. Rep. 1894, **18**, 194; Ber. 1894, **27**, R, 665; Bull. Soc. Chim. 1894, **11**, 949; Mon. Sci. 1894, **43**, 717; Chem. News, 1894, **70**, 72, 282; Rev. gén. sci. 1894, **5**, 552; Jahr. organ. Chem. 1894, **2**, 219.

[4] W. Bone and D. Jerden, J. C. S. 1897, **71**, 41; 1901, **79**, 1042; abst. Chem. News, 1896, **73**, 151; **74**, 268; J. S. C. I. 1901, **20**, 696; Bull. Soc. Chim. 1898, **18**, 986; Chem. Centr. 1897, **68**, I, 24, 582; 1901, **72**, II, 394, 576; Jahr. Chem. 1901, **54**, 570.

[5] W. Bone and H. Coward, J. C. S. 1908, **93**, 1197; 1910, **97**, 1975; 1909, **98**, 20, 265; abst. J. S. C. I. 1908, **27**, 1143; 1910, **29**, 744; Bull. Soc. Chim. 1909, **6**, 874, 1355; 1911, **10**, 566; Chem. Zentr. 1908, **79**, II, 763; 1909, **80**, I, 350; 1910, **81**, II, 442; Jahr. Chem. 1905–1908, II, 78.

[6] J. prakt. Chem. 1886, **141**, 321; Ber. 1887, **20**, 141, 3039; 1889, **22**, 475, 478; abst. J. C. S. 1887, **52**, 459; 1889, **56**, 581; J. S. C. I. 1887, **6**, 446;

yield a sweet syrup, called by him formose; or with magnesium oxide, a product called methose. Later, E. Fischer showed this formose and methose to be complex mixtures containing α-acrose.[1]

On distilling dry starch with lime[2] in the proportion of 1–4, acetone, mesityl oxide, isophorone boiling at 207°, and various acetone condensation bodies result. When distilled with MnO_2 and dilute H_2SO_4, formic acid, furfural and CO_2 result. Distilled with HCl and MnO_2, there is formed—among other things—trichloracetaldehyde and pentachlor-porpionicaldehyde.

Soluble and Modified Starch. In recent years a class of "thin boiling" or "modified" starches have been used in the treatment of textiles, which support their claim for recognition on the fact that they are of low viscosity and can be prepared readily without tedious preliminary heat treatment.

The Casein Co. of America[3] modify starch by treatment first with oxalic acid followed by ammonia when the action has proceeded to the desired point. When the viscosity has reached a predetermined value after the neutralization, the product is dried and is then ready for the market. L. Cerf,[4] by the use of persulfates; Arabol Manufacturing Co. with sulfocyanides;[5] and

---

1889, **8**, 297; Bull. Soc. Chim. 1888, **49**, 712; 1890, **3**, 709, 712; Chem. Centr. 1887, **58**, 229; 1889, **60**, I, 465, 466; Jahr. Chem. 1887, **40**, 2247; 1889, **42**, 2034. A. Butlerow, Ann. 1861, **120**, 295; Compt. rend. 1861, **53**, 145; abst. Bull. Soc. Chim. 1861, **2**, 84; Instit. 1861, 260; Rep. Chim. Pure, 1861, **3**, 404; Chem. Centr. 1861, **32**, 686; Jahr. Chem. 1861, **14**, 647; Zts. Chem. 1861, 462.

[1] E. Fischer and J. Tafel, Ber. 1887, **20**, 2568; abst. J. C. S. 1888, **54**, 39, 358; J. S. C. I. 1888, **7**, 128; 1889, **8**, 296; Bull. Soc. Chim. 1888, **49**, 359, 972; J. pharm. chim. 1889, (5), **20**, 411; Chem. Centr. 1887, **58**, 1491; Jahr. Chem. 1887, **40**, 1283. E. Fischer, Ber. 1890, **23**, 386, 2114; abst. J. C. S. 1890, **58**, 466, 1223; J. S. C. I. 1890, **9**, 527, 958; Bull. Soc. Chim. 1890, **3** 891; J. pharm. chim. 1890, (5), **22**, 376, 401; Chem. Centr. 1890, **61**, I, 640; II, 430; Jahr. Chem. 1890, **43**, 2116, 2130.

[2] V. Horvat, Rad. jugost. akad. **75**, 187; abst. J. C. S. 1887, **52**, 460; Chem. Centr. 1887, **58**, 38; Jahr. Chem. 1887, **40**, 2262.

[3] U. S. P. 1053719, 1913; abst. C. A. 1913, **7**, 1287; Kunst. 1913, **3**, 256. F. P. 454456, 1913; abst. Chem. Ztg. Rep. 1913, **37**, 577. E. P. 4203, 1913; abst. C. A. 1914, **8**, 2804; J. S. C. I. 1913, **32**, 302.

[4] U. S. P. 698632, 1902; abst. J. S. C. I. 1902, **21**, 784; Mon. Sci. 1902, **58**, 190.

[5] D. R. P. 180830; abst. Chem. Zentr. 1907, **78**, II, 200; Chem. Ztg. Rep. 1907, **31**, 108; Jahr. Chem. 1905–1908, II, 2940; Wag. Jahr. 1907, **53**, II, 213; Zts. ang. Chem. 1907, **20**, 1781. D. R. P. 221797; abst. Chem. Zentr. 1910, **81**, I, 2002; Chem. Ztg. Rep. 1910, **34**, 250; Jahr. Chem. 1910, **63**, II, 410; Wag. Jahr. 1910, **56**, II, 259; Zts. ang. Chem. 1910, **23**, 1248. Aust. P. 29738, 39015. E. P. 7705, 1905; abst. J. S. C. I. 1906, **25**, 944. U. S. P. 918925, 1907; abst. Chem. Ztg. Rep. 1909, **33**, 272. F. P. 365161, 1906; abst. Mon. Sci. 1907, **67**, 99. F. P. 394167, 1908; abst. Mon. Sci. 1909, **71**, 146. E. P.

others[1] by employing perborates accomplish a similar result, accompanied by a whitening of the product through the bleaching action of the per-salt. Gaseous HCl in the hands of F. Frary and A. Dennis;[2] oxalic acid as manipulated by H. Dierssen;[3] sulfur dioxide under pressure;[4] treatment with alkaline permanganates,[5] or less often with chromic acid.[6] Ozone does not act upon starch.[7]

The methods of P. Bean,[8] and the apparatus of A. Lenders[9] should also be mentioned.

The "thin boiling" starches as perfected by C. Duryea[10] and

---

17887, 17888, 1908; abst. J. S. C. I. 1909, **28**, 996; J. Soc. Dyers Col. 1909, **25**, 283. Aust. P. 39015.

[1] Stoll & Kopke, D. R. P. 199753; abst. Chem. Zentr. 1908, **79**, II, 551; Chem. Ztg. Rep. 1908, **32**, 391; Jahr. Chem. 1905–1908, II, 941; Wag. Jahr. 1908, **54**, II, 190; Zts. ang. Chem. 1908, **21**, 1805. D. R. P. 202229; abst. Chem Zentr. 1908, **79**, II, 1478; Chem. Ztg. Rep. 1908, **32**, 558; Chem. Zts. 1909, **8**, 1139; Jahr. Chem. 1905–1908, II, 941; Wag. Jahr. 1908, **54**, II, 191. E. P. 30390, 1909; abst. J. S. C. I. 1910, **29**, 1200. F. Fritzsche, E. P. 1351, 1908; abst. J. S. C. I. 1908, **27**, 869; C. A. 1909, **3**, 600. U. S. P. 910524, 1909. Stoll & Kopke, Aust. P. 37835, 37836, 40449, 42647.

[2] J. Ind. Eng. Chem. 1915, **7**, 214; abst. C. A. 1915, **9**, 1132; J. S. C. I. 1915, **34**, 440.

[3] Zts. ang. Chem. 1903, **16**, 122; Mon. Sci. 1903, **59**, 779; abst. J. C. S. 1903, **84**, i, 321; J. S. C. I. 1903, **22**, 312; Rep. Chim. 1903, **3**, 201; Chem. Centr. 1903, **74**, I, 698; Jahr. Chem. 1903, **56**, 995; Wag. Jahr. 1903, **49**, II, 216.

[4] W. Thomson and J. Morrice, E. P. 21973, 1906; abst. J. S. C. I. 1907, **26**, 980. U. S. P. 951666; abst. J. S. C. I. 1908, **27**, 444; Chem. Ztg. Rep. 1910, **34**, 200.

[5] O. Bredt & Co., D. R. P. 149588; abst. Chem. Centr. 1904, **75**, I, 976; Chem. Ztg. 1904, **28**, 329; Jahr. Chem. 1905–1908, II, 941; 1904, **57**, 1153; Wag. Jahr. 1904, **50**, II, 222; Zts. ang. Chem. 1904, **17**, 935. D. R. P. 156148; abst. Chem. Centr. 1905, **76**, I, 643; Chem. Ind. 1904, **27**, 704; Chem. Ztg. 1904, **28**, 1236; Jahr. Chem. 1905–1908, II, 940; Wag. Jahr. 1904, **50**, II, 223; Zts. ang. Chem. 1905, **18**, 349. Aust. P. 20714, 1905. E. P. 22370, 1903; abst. J. S. C. I. 1904, **23**, 29; J. Soc. Dyers Col. 1904, **20**, 38.

[6] E. Harz, Beiheft. z. Botan. Centr. 1905; Woch. f. Brau. 1905, **22**, 721; abst. J. S. C. I. 1905, **24**, 1315.

[7] E. Gorup-Besanez, Mitt. Phys. Med. Soc. 1859, **1**, 13; Chem. News, 1863, **8**, 222; J. pharm. Chim. 1859, **36**, 65; Ann. 1859, **110**, 103; 1863, **125**, 207; abst. Rep. Chim. Pure, 1858–1859, **1**, 408.

The process of L. Koenig (E. P. 9674, 1894; abst. J. S. C. I. 1894, **13**, 824) deodorizes and bleaches amylaceous materials such as starch, by means of ozone.

[8] J. Text. Inst. 1915, **4**, 223; abst. J. S. C. I. 1916, **35**, 107; C. A. 1916, **10**, 392.

[9] U. S. P. 948512, 948513, 1159591, 1159592, 1168516, 1191324. 1193274, 1223406; abst. J. S. C. I. 1910, **29**, 367; 1915, **34**, 1265; 1916, **35**, 937.

[10] E. Duryea, U. S. P. 172099, 345417, 345418, 375737. H. Duryea, U. S. P. 12846, 300700, 301436. W. Duryea, U. S. P. 22789, 42358, 263030, 312341, 312342, 320430, 320431, 340705. C. Duryea, U. S. P. 643323, 658105, 696949. E. P. 2459, 1900; 11442, 1901; 11801, 1907; abst. J. S. C. I. 1900, **19**, 455; 1901, **20**, 1127. F. P. 380680, 1907; abst. J. S. C. I. 1908, **27**, 32; 1911, **30**, 789.

W. Nivling,[1] are obtained by careful treatment of raw starch for some hours with a dilute mineral acid, preferably sulfuric, then washing to neutrality and drying. They have had a wide sale in the United States, especially for the stiffening of textiles and for laundry purposes.

According to O. Schmerber,[2] starch oxidized with potassium permanganate gives a paste more fluid and transparent than that which is obtained from the same starch in the ordinary state. On standing, permanganate oxidized starch becomes opaque, but reassumes its transparency when heated. E. Dollfus and F. Scheurer[3] find that the starch paste appears to be closely related to soluble starch. W. v. Siemens[4] also purifies starch with permanganate. Siemens & Halske[5] and F. Hermite[6] oxidize and thin starch by electrolysis of a solution of sodium or magnesium chlorides, starch so produced being very clear and white. C. Lintner[7] mentions that the course of thinning agents on starch, such as the permanganates, can be followed by testing with iodine solution, as is done in the process of converting starch into diastase, the colors obtained with iodine at successive stages of such action with potassium permanganate being blue-violet, violet-red, and reddish brown. At the final stage of oxidation, no color is produced. The products obtained are gummy substances which are differentiated from the dextrins by their reactions and by their yielding a precipitate with basic lead acetate and with barium hydroxide. On boiling they expel CO_2, and slightly reduce Fehling's solution. C. Gerber uses hydrogen peroxide,[8]

---

[1] U. S. P. 1153244, 1153245, 1191216, 1236002, 1918. E. P. 10866, 1916. Can. P. 164541.

[2] Bull. Soc. Ind. Mulhouse, 1896, 238; abst. J. S. C. I. 1896, **15**, 649.

[3] Bull. Soc. Ind. Mulhouse, 1896, 241; abst. J. S. C. I. 1896, **15**, 649.

[4] E. P. 2597, 1893. Aust. P. 19777, 1905. D. R. P. 70012, 1892; 97565; abst. J. S. C. I. 1894, **13**, 34; 1896, **15**, 366. C. Siemens, Dingl. Poly. 1842, **84**, 390; 1864, **172**, 232; Bull. Soc. Ind. Mulhouse, 1893, 363. Zts. f. Spiritsind. 1893, 253; 1898, **21**, 59; abst. J. S. C. I. 1898, **27**, 257.

[5] O. Witt, assignor to Siemens & Halske, E. P. 24455, 1895. D. R. P. 88447, 1895. U. S. P. 798509; Chem. Ind. 1909, **32**, 68; J. S. C. I. 1896, **15**, 366; 1905, **24**, 1024. Chem. Ind. 1909, **32**, 68. Cf. Soc. des Produits Amylaces, Swiss P. 32790, 1904, who also purify starch electrically.

[6] E. P. 1061, 1892; abst. J. S. C. I. 1893, **12**, 168. E. Hermite and A. Dubosc, D. R. P. 70275; Zts. f. Spiritsind. 1893, 262, 409, 417. E. Hermite, E. Paterson and C. Cooper, E. P. 12906, 1889; abst. J. S. C. I. 1890, **19**, 878.

[7] Zts. ang. Chem. 1890, **3**, 546; abst. J. C. S. 1891, **60**, 537; Ber. 1890, **23**, R, 701; Chem. Centr. 1890, **61**, II, 690; Jahr. Chem. 1890, **43**, 2151; Wag. Jahr. 1890, **36**, 819.

[8] Compt. rend. 1912, **154**, 1543; abst. J. C. S. 1912, **102**, i, 538; J. S. C. I. 1912, **31**, 654. Bied. Centr. 1913, **42**, 265; Compt. rend. Soc. Biol.

and A. v. Asboth[1] and A. Fernbach and J. Wolff,[2] H_2O_2 and ammonia, obtaining by this action a thin starch paste from which soluble starch (amylodextrin) may be precipitated by alcohol, the amount approaching, in extreme instances, 80% of the original product. In all these treatments, the viscosity is considerably attenuated, and the solubility in water increased. Hence the name "soluble" starches.

O. Durieux[3] claims that hydrogen peroxide does not hydrolyze starch prepared by Fernbach's method at ordinary temperature, and the same is true of colloidal solutions of iron or of mixtures of these two. Ferric chloride alone, also has no action, but in conjunction with H_2O_2, hydrolysis takes place, which increases with the quantity of ferric chloride used.[4]

Z. Gatin-Gruzewska[5] has followed the course of the oxidation and hydrolysis of starch by hydrogen peroxide, and finds that hydrolysis and oxidation take place simultaneously, the final products being maltose and oxalic acid. The constituents of starch—amylopectin and amylose—are acted upon in a different manner by hydrogen peroxide (as they are by diastase). In the case of both, dextrins are formed as intermediate products. With amylopectin, the attack on the micellae appears to be simultaneous; in that of amylose, successive.

F. Urech[6] has studied the rate of oxidation of starch by means of Fehling's solution, P. Petit,[7] oxidation by means of

1911, **70**, 139, 391, 547, 724, 726, 728; J. C. S. 1913, **104**, i, 781. Compare, P. Bergh and H. Neuberger, U. S. P. 1133914, 1915; abst. J. S. C. I. 1915, **34**, 567.

[1] Chem. Ztg. 1892, **16**, 1517, 1560; abst. J. C. S. 1893, **64**, i, 384; Chem. Centr. 1892, **63**, II, 867; Jahr. Chem. 1892, **45**, 2467.

[2] Compt. rend. 1904, **138**, 1217; 1905, **140**, 1067, 1547; Seventh Intl. Cong. Appl. Chem. 1909, VI-B, 124; abst. J. C. S. 1905, **88**, i, 312, 574, 624; 1911, **100**, i, 356.

[3] Bull. Soc. Chim. Belg. 1913, **27**, 90; abst. J. C. S. 1913, **104**, i, 445; C. A. 1913, **7**, 3552; J. S. C. I. 1913, **32**, 440; Chem. Zentr. 1913, **84**, I, 1870.

[4] C. Neuberg and S. Miura, Biochem. Zts. 1911, **36**, 37; abst. J. C. S. 1911, **100**, i, 935; C. A. 1912, **6**, 374; Bull. Soc. Chim. 1912, **12**, 692; Chem. Zentr. 1911, **82**, II, 1605. C. Gerber, Compt. rend. 1912, **154**, 1543; abst. J. C. S. 1912, **102**, i, 538; J. S. C. I. 1912, **31**, 654; Bull. Soc. Chim. 1912, **11**, 988; Chem. Zentr. 1912, **83**, II, 244; Meyer Jahr. Chem. 1912, **22**, 430.

[5] Compt. rend. 1908, **146**, 540; 1909, **148**, 578; abst. J. C. S. 1908, **94**, i, 320; 1909, **96**, i, 209; J. S. C. I. 1909, **28**, 376; C. A. 1909, **3**, 1410; 1910, **4**, 3082; Chem. Zentr. 1909, **80**, I, 1231; Jahr. Chem. 1909, **62**, II, 377.

[6] Ber. 1884, **17**, 495, 1539; abst. J. S. C. I. 1884, **3**, 451; J. C. S. 1884, **46**, 574, 1112; Jahr. Chem. 1884, **37**, 1403.

[7] Compt. rend. 1892, **114**, 1375; 1897, **125**, 355; 1905, **141**, 1247; abst. J. C. S. 1892, **62**, 1171; 1906, **90**, i, 67; J. S. C. I. 1897, **16**, 1028. For

nitric acid, and some other of the inorganic acid compounds.

Many of the processes put forward from time to time for the formation of modified starches, are applicable for the manufacture of soluble starch, by allowing the process to continue until the stage of water miscibility has been reached. It is customary to treat the starch with a mineral acid, care being taken that the acid concentration and temperature is so controlled that loss of starch by dextrin formation is reduced to the minimum.

T. Bayley[1] and F. Virneisel[2] use sulfuric acid, the former of 7%–8% strength, and the latter of 1%–2% acid, at a temperature of 50°–55° until conversion is complete. W. Angele,[3] R. Chapin[4] and O. Foerster,[5] employ hydrochloric acid, while phosphoric,[6] hydrofluoric, chloric,[7] phosphotungstic,[8] and formic acids[9] have been advocated for this purpose. It has been shown that with dry starch and gaseous HCl[10] at temperatures within 20°–100°,

treatment of starch with aluminum or ferric chlorides, see D. R. P. 217336; abst. Wag. Jahr. 1910, **56**, II, 259; Chem. Zentr. 1910, **81**, II, 492; Chem. Ztg. Rep. 1910, **34**, 46; Zts. ang. Chem. 1910, **23**, 910. The thin boiling starch of T. Breyer, is described in U. S. P. 881104, 881105, 1908; abst. Chem. Ztg. Rep. 1908, **32**, 300. For the non-gelatinizable starch of B. Herstein, U. S. P. 982673, 1911; abst. J. S. C. I. 1911, **30**, 301; Chem. Ztg. Rep. 1911, **35**, 181. A. Leulier, J. pharm. chim. 1918, **18**, 291; abst. C. A. 1919, **13**, 915; J. S. C. I. 1919, **38**, 86-A. M. Witlich, Kunst. 1912, **2**, 62. Otto Bredt & Co., U. S. P. 769061, 1904. T. Breyer, U. S. P. 881104, 1908. A. Lenders, U. S. P. 1305291, 1919; abst. J. S. C. I. 1919, **38**, 593-A. E. Blumer, E. P. 10872, 1902; F. P. 322206, 1902; D. R. P. 137330; Aust. P. 14886, 1904; abst. J. S. C. I. 1903, **22**, 310. C. Hervey, E. P. 20484, 1908; abst. J. S. C. I. 1909, **28**, 1157. Casein Co., E. P. 4203, 1913. W. and S. Elborn and A. Board, E. P. 16997, 1913; abst. J. S. C. I. 1914, **33**, 935.

[1] E. P. 20930, 1893; abst. J. S. C. I. 1894, **13**, 1082.

[2] E. P. 12020, 1898; abst. J. S. C. I. 1899, **18**, 697. Aust. P. 2023, 1900. Rev. Prod. Chim. **2**, 273; abst. J. S. C. I. 1900, **19**, 548. Pap. Fab. 1909, **7**, 335; abst. J. S. C. I. 1909, **28**, 439. L. and F. Virneisel, K. Trobach and A. Cords, D. R. P. 33189, 1884; abst. Wag. Jahr. 1885, **31**, 659.

[3] E. P. 5617, 1893; abst. J. S. C. I. 1894, **13**, 265. D. R. P. 4702, 1878; 15354, 16221, 1880; abst. Wag. Jahr. 1881, **27**, 579; 1882, **28**, 682.

[4] J. Ind. Eng. Chem. 1914, **6**, 649; abst. J. C. S. 1914, **106**, ii, 739; C. A. 1914, **8**, 3401.

[5] Chem. Ztg. 1897, **21**, 41; abst. J. S. C. I. 1897, **16**, 251; J. C. S. 1898, **74**, i, 61; Chem. Centr. 1897, **68**, I, 408; Jahr. Chem. 1897, **50**, 1518.

[6] G. Rivat, F. P. 433726, 1910; abst. J. S. C. I. 1912, **31**, 245; J. Soc. Dyers Col. 1912, **28**, 84.

[7] A. Ashworth, E. P. 19720, 1901; abst. J. S. C. I. 1902, **21**, 1288; J. Soc. Dyers Col. 1902, **18**, 274; Chem. Ztg. 1903, **27**, 104. F. Mirow, D. R. P. 273235, 1913; abst. J. S. C. I. 1914, **33**, 761; Wag. Jahr. 1914, **60**, II, 460; Chem. Zentr. 1914, **85**, I, 1720; Chem. Ztg. Rep. 1914, **38**, 289; Zts. ang. Chem. 1914, **27**, 387; C. A. 1914, **8**, 2825.

[8] K. Huppert, Zts. physiol. Chem. 1893–1894, **18**, 247.

[9] N. Welwart, Chem. Ztg. 1907, **31**, 126; abst. J. S. C. I. 1907, **26**, 216; Chem. Zentr. 1907, **78**, I, 1467.

[10] F. Frary and A. Dennis, J. Ind. Eng. Chem. 1915, **7**, 214; abst. J. C. S. 1916, **110**, i, 202; C. A. 1915, **9**, 1132; J. S. C. I. 1915, **34**, 440.

for a given acidity there is a definite temperature range within which heating for 30 minutes will convert starch into the soluble variety. At higher temperatures the starch is rapidly converted into dextrin. It has also been determined that for a given temperature, range of acidity within which a soluble starch is produced is well defined, and that the use of larger quantities of acid result in the formation of dextrin, while with a smaller amount, the starch fails to become soluble.

E. Kunz is authority for the statement that the action of HF is but one-seventeenth as great as HCl in the preparation of soluble starch.[1] Heat alone may be used for its preparation,[2] a temperature of 140° for 3 hours at 2.5 atmospheres pressure giving excellent results.[3] When the starch is heated with the acid in the form of vapor[4] a lower temperature, it is claimed, may be employed, and less danger of the formation of dextrins.[5]

Hypochlorites[6] or chlorine,[7] the action being facilitated by the presence of catalytic agents such as the salts of cobalt, copper, iron, manganese and nickel, form the novelty claims of recent patents.[8] The duration of treatment is governed by the desired solubility, complete solubility in hot water being claimed after three to four hours heating at 50°. Copper sulfate in connec-

---

[1] Zts. Spiritusind. 1915, **38**, 295; abst. J. C. S. 1916, **110**, i, 202; Chem. Zentr. 1915, **87**, II, 783; C. A. 1915, **9**, 3375. Cf. E. Deussen, Zts. anorg. Chem. 1905, **44**, 300, 408; abst. J. C. S. 1905, **88**, ii, 311; J. S. C. I. 1905, **24**, 440, 496; Chem. Centr. 1905, **76**, I, 1208, 1298; Jahr. Chem. 1905–1908, I, 1441, 1442.

[2] P. Thomas, Ann. de la Brass. **5**, 267; abst. J. S. C. I. 1902, **21**, 1033.

[3] A. Fielding, E. P. 20488, 1906; abst. J. S. C. I. 1907, **26**, 980.

[4] W. Browning and J. Barlow, U. S. P. 773469, 773783, 1904; abst. Mon. Sci. 1905, **63**, 65. E. P. 19499, 1903; abst. J. S. C. I. 1904, **23**, 795; J. Soc. Dyers Col. 1904, **20**, 200. F. P. 336903, 1903; abst. J. S. C. I. 1904, **23**, 449; J. Soc. Dyers Col. 1904, **20**, 84.

[5] F. Fol, D. R. P. 119265, 1901; abst. Wag. Jahr. 1901, **47**, II, 275; Chem. Centr. 1901, **72**, I, 924; Chem. Ztg. 1901, **25**, 413; Mon. Sci. 1901, **57**, 217; 1905, **63**, 820. Aust. P. 6251, 1901.

[6] A. and H. Haake, U. S. P. 813647, 1906; abst. J. S. C. I. 1906, **25**, 276. E. P. 885, 1903; abst. J. S. C. I. 1903, **22**, 754; F. P. 326286, 1902; abst. J. S. C. I. 1903, **22**, 812. D. R. P. 114973, abst. Wag. Jahr. 1900, **46**, II, 371. Aust. P. 26366, 1906.

[7] H. Kindscher, D. R. P. 149588, 168980; abst. Wag. Jahr. 1904, **50**, II, 222; 1906, **52**, II, 223; Chem. Centr. 1904, **75**, I, 976; 1906, **77**, I, 1514; Chem. Ztg. 1904, **28**, 329; 1906, **30**, 304; Zts. ang. Chem. 1904, **17**, 935; 1907, **20**, 364; Jahr. Chem. 1904, **57**, 1153; 1905–1908, II, 721, 941; Mon. Sci. 1908, **69**, 47.

[8] A. Paira and Administration der Minen von Buchsweiler Akt. Ges. E. P. 9370, 1909; abst. J. S. C. I. 1909, **28**, 950. F. P. 402060, 1909; abst. Mon. Sci. 1912, **77**, 176.

tion with the injection of a current of air is said to admit of soluble starch being produced in an hour at a temperature not exceeding 40°–50°.[1] E. Flick[2] hastens the time of action by the use of nascent oxygen liberated from persulfates, in the presence of small amounts of aluminium, iron or zinc chlorides.[3] The "Societe Trust Chimique" also make use of this method.[4] The use of aluminium chloride,[5] is claimed to prevent or at least retard, the extraction of objectionable nitrogenous matter.[6]

The soluble starch of R. Ansarge[7] comprizes the addition of borax, zinc white and stearin, that of C. Perkins[8] of borax, salt and wax. Others use ozone,[9] sodium thiosulfate and aluminium salts,[10] or sulfonated fatty acid (Turkey red oil),[11] the latter making a smoother preparation, and one which penetrates textiles more easily.

The soluble starch of K. Zulkowski[12] is based upon the observation that glycerol at 190° is capable of dissolving 6% of powdered starch and converting it into a soluble modification.

---

[1] J. Dufour, Ann. Agronom, **12**, 297; Bull. Soc. Vaudoise de Sci. Nat. **21**, No. 93; abst. J. C. S. 1886, **50**, 903; Arch. ph. Nat. (3), 1886, **15**, 439; Jahr. Chem. 1886, **39**, 1809.

[2] E. P. 25121, 1909; abst. J. S. C. I. 1910, **29**, 444; J. Soc. Dyers Col. 1910, **26**, 133. F. P. 406084, 1909; abst. Mon. Sci. 1911, **75**, 150. D. R. P. 217336, 1910; abst. Wag. Jahr. 1910, **56**, II, 259; Chem. Zentr. 1910, **81**, I, 492; Chem. Ztg. Rep. 1910, **34**, 46; Zts. ang. Chem. 1910, **23**, 910; Chem. Zts. 1910, **9**, No. 1729. Aust. P. 50004, 1911. Swiss P. 50220, 1909.

[3] T. Myers, E. P. 23554, 1896; abst. J. Soc. Dyers Col. 1896, **12**, 237.

[4] D. R. P. 134301, 1901; abst. Zts. ang. Chem. 1902, **15**, 1019; J. S. C. I. 1902, **21**, 1288; Wag. Jahr. 1902, **48**, II, 300; Chem. Centr. 1902, **73**, II, 836; Chem. Ztg. 1902, **27**, 901; Jahr. Chem. 1902, **55**, 1037; Chem. Zts. 1903, **2**, 281.

[5] Soc. Anon. Alliance Industrielle, E. P. 8514, 1900; abst. J. S. C. I. 1901, **20**, 492; Chem. Ztg. 1901, **25**, 780; Mon. Sci. 1902, **58**, 162.

[6] J. S. C. I. 1905, **24**, 358. See also B. Federer, Chem. Ztg. 1903, **27**, 925; abst. J. S. C. I. 1903, **22**, 1142.

[7] E. P. 586, 1897; abst. J. S. C. I. 1897, **16**, 928. See also W. Zwick, E. P. 12326, 1884; abst. J. S. C. I. 1885, **4**, 237. D. R. P. 29975, 1884; abst. Wag. Jahr. 1885, **31**, 969.

[8] U. S. P. 1149216, 1915; abst. C. A. 1915, **9**, 2722.

[9] E. Eckland, U. S. P. 1000726, 1911; abst. J. S. C. I. 1911, **30**, 1130; Chem. Ztg. Rep. 1911, **35**, 454.

[10] W. D'Rohan, U. S. P. 1248092, 1917; abst. C. A. 1918, **12**, 298.

[11] E. Weingaertner, U. S. P. 984330, 1911; abst. C. A. 1911, **5**, 1534.

[12] Ber. 1880, **13**, 1395; abst. J. C. S. 1880, **38**, 865; Chem. News, 1877, **35**, 8; 1882, **45**, 130; Bull. Soc. Chim. 1881, **36**, 271; J. pharm. chim. 1880, **2**, 494; Chem. Tech. Rep. 1878, **17**, I, 298; Jahr. Chem. 1880, **33**, 1005. Oesterr. Ges. Chem. Ind. **10**, 2; abst. Chem. Centr. 1888, **59**, 1060; J. C. S. 1889, **56**, 116; Jahr. Chem. 1888, **41**, 2322. Ber. 1890, **23**, 3295; abst. J. C. S. 1891, **60**, 165; J. S. C. I. 1891, **10**, 56; Bull. Soc. Chim. 1891, **6**, 679; Jahr. Chem. 1890, **43**, 2151.

This may readily be prepared by heating potato starch with glycerol at 180°–190° for one-half hour, or for a longer time with rice starch, the solution, after being allowed to cool down to 120°, is poured into a large volume of alcohol, and the soluble product washed with cold water and dried.[1]

A continuous process has been evolved[2] in which the starch is passed over a heated surface, the temperature and time of contact of starch with the heat being so adjusted as to give a water-soluble final product.

According to C. Tanret,[3] when soluble starch is prepared by J. Wolff's method,[4] a sparingly soluble product is also formed resembling the amylocellulose of L. Maquenne and E. Roux.[5] This apparently is not a single substance, as shown by fractional precipitation with alcohol of its aqueous solution.[6]

A. Reychler[7] has subjected the results of E. Fouard[8] on the

[1] F. Aspinall, E. P. 9106, 1903; abst. J. S. C. I. 1904, **23**, 618.

[2] U. S. P. 578566, 1897; 785216, 1905; 984483, 1911; 1207177, 1916; abst. J. S. C. I. 1906, **25**, 998; 1917, **36**, 156. E. P. 5844, 1896; 5574, 1904; 10216, 1906; 3004, 3414, 3415, 1910; 9082, 1912; abst. J. S. C. I. 1896, **15**, 605; 1905, **24**, 144; 1910, **29**, 1468; 1913, **31**, 788. F. P. 343614, 1904; 365834, 1906; 442619; abst. J. S. C. I. 1904, **23**, 1038; 1906, **25**, 998; 1912, **31**, 788. D. R. P. 88648, 147896, 158861, 166259, 227430. Aust. P. 21431, 1905; 24085, 1906; 56825, 56861, 56862, 1912; 63956, 1914. See also E. Oeser, E. P. 19549, 1899. Aust. P. 52338, 1912.

[3] Compt. rend. 1909, **148**, 1775; abst. J. C. S. 1909, **96**, i, 556; C. A. 1909, **3**, 2676; J. S. C. I. 1909, **28**, 847; Bull. Soc. Chim. 1909, **5**, 902; Rep. Chim. 1909, **9**, 256; Chem. Zentr. 1909, **80**, II, 592, 1637; Jahr. Chem. 1909, **62**, II, 374; Wag. Jahr. 1909, **55**, II, 226; Zts. ang. Chem. 1909, **22**, 2345.

[4] Compt. rend. 1905, **140**, 1403; abst. J. C. S. 1905, **88**, i, 510; Chem. Centr. 1905, **76**, II, 121; Jahr. Chem. 1905–1908, II, 938.

[5] Compt. rend. 1905, **140**, 1303; abst. J. C. S. 1905, **88**, i, 511; Chem. News, 1905, **91**, 279; J. S. C. I. 1905, **24**, 630; Bull. Soc. Chim. 1905, **33**, 723; Rep. Chim. 1905, **5**, 318; Chem. Centr. 1905, **76**, II, 121, 314; Chem. Zts. 1906, **5**, 10; Meyer Jahr. Chem. 1905, **15**, 410; Biochem. Centr. 1905–1906, **4**, 138, 380; Tech. Chem. Jahr. 1905, **28**, 274.

[6] F. Musculus, Compt. rend. 1874, **78**, 1413; abst. J. C. S. 1874, **27**, 1077, 1174; Chem. News, 1874, **30**, 20; Ann. Chim. Phys. 1874, (5), **2**, 385; J. pharm. chim. 1874, **20**, 39; Ber. 1874, **7**, 824; Chem. Tech. Rep. 1874, **13**, II, 152; Dingl. Poly. 1874, **214**, 407; Jahr. Chem. 1874, **27**, 881; Jahr. rein Chem. 1874, **2**, 177; Wag. Jahr. 1874, **20**, 651; 1875, **21**, 771; Amer. Chemist, 1875, **5**, 192; Springm. Musterztg. 1875, 113.

[7] Bull. Soc. Chim. Belg. 1909, **23**, 378; abst. J. S. C. I. 1909, **28**, 1216; J. C. S. 1909, **96**, ii, 977; Chem. Zentr. 1909, **80**, II, 2140; J. Chim. Phys. 1909, **7**, 497, 362; 1910, **8**, No. 1.

[8] Compt. rend. 1907, **144**, 501; 1908, **146**, 285, 978; **147**, 931; 1909, **148**, 502; Bull. Soc. Chim. 1909, **5**, 828; abst. J. C. S. 1907, **92**, i, 391, 677; 1908, **94**, i, 138, 503, 953; 1909, **96**, i, 13, 209; J. S. C. I. 1907, **26**, 832; 1908, **27**, 238, 635, 1215; 1909, **28**, 433, 898; Chem. Zentr. 1907, **78**, I, 1029; II, 391; 1908, **79**, I, 1264; II, 1098, 2000; 1909, **80**, I, 68, 644, 1091, 1987; II, 974; Jahr. Chem. 1905–1908, II, 937, 939, 940.

absorption of certain bases by soluble starch to careful analysis, and finds that the reactions between soluble starch and bases take place according to Guldberg and Waage's law of mass action, and are therefore chemical in nature. He considers these starch compounds as similar to alcoholates.[1] E. Fouard, however, has shown[2] that the addition of alkalis to solutions of the various polysaccharides cause a progressive alteration in the optical rotatory power, usually explained by the gradual neutralization of their acid groups, since definite chemical compounds are precipitated by the addition of a large excess of alcohol. He apparently has demonstrated[3] that the progressive "solubilization" of colloidal starch by alkalis is accompanied by a corresponding change in the rotatory power of the solution—a change which appears quantitative. His conclusion is that the action of alkalis upon starch is a process of subdividing the granules of the colloid to a high degree, at the same time modifying them optically, and being fixed by them in a variable proportion. This extremely complex phenomenon is neither purely chemical or entirely physical, but rather an intramolecular change.

Whereas the term "soluble starch" and "amylodextrin" have been employed as synonymous, A. Wroblewski[4] restricts the former to the first decomposition product of starch which gives a blue coloration with iodine and does not reduce Fehling's solution. Amylodextrin is more properly to be regarded as a decomposition product of soluble starch; iodine colors it reddish brown and it somewhat reduces Fehling's solution.

W. Syniewski[5] has examined the soluble starch obtained by

[1] J. Kraus, Ann. Agronom, **12,** 540; abst. J. C. S. 1887, **52,** 173; Chem. News, 1887, **55,** 69.

[2] Bull. Soc. Chim. 1909, **5,** 828; abst. J. C. S. 1909, **96,** i, 699; J. C. S. 1909, **96,** i, 13, 209; Chem. Zentr. 1909, **80,** I, 68, 644, 1091, 1987; II, 974; Jahr. Chem. 1905–1908, II, 937, 939, 940.

[3] Compt. rend. 1909, **148,** 502; abst. J. C. S. 1909, **96,** i, 209; Chem. Zentr. 1909, **80,** II, 974; Jahr. Chem. 1905–1908, II, 939, 940. See also Erste Triester Reisschäl-Fabriks Akt. Ges. E. P. 4719, 1908. F. P. 387736, 1908; abst. J. S. C. I. 1908, **27,** 854, 938.

[4] Ber. 1897, **30,** 2108; Chem. Ztg. 1898, **22,** 375; abst. J. C. S. 1898, **74,** i, 8; 1899, **76,** i, 324; J. S. C. I. 1897, **16,** 1028; 1898, **17,** 778; Bull. Soc. Chim. 1898, **20,** 302; Chem. Centr. 1897, **68,** II, 842; 1898, **69,** II, 19; Jahr. Chem. 1897, **50,** 1518; 1898, **51,** 1353; Wag. Jahr. 1897, **43,** 788.

[5] Ber. 1897, **30,** 2415; 1898, **31,** 1791; abst. J. C. S. 1898, **74,** i, 61, 551; J. S. C. I. 1897, **16,** 1029; 1898, **17,** 778; Bull. Soc. Chim. 1898, **20,** 367; 1899, **22,** 223; Chem. Centr. 1897, **68,** II, 1107; 1898, **69,** II, 421; Jahr. Chem 1897, **50,** 1518; 1898, **51,** 1354.

treating ordinary starch with sodium peroxide, which was found to be insoluble in water, but when washed with water, alcohol and ether and carefully dried, gave numbers indicating a derivative of soluble starch with the elements of water removed. When treated with baryta water a product of the composition $C_{18}H_{25}O_{16}(C_2H_3O)_7$ was formed upon acetylation, and an analogous benzoyl compound was also isolated. Soluble starch could not be regenerated by hydrolysis of the acetyl derivative. By HCl inversion, an amount of glucose equivalent to 99.3% was obtained on the assumption that soluble starch has the formula $C_{18}H_{32}O_{16}$. The invertive action of water under pressure on soluble starch is light, but a freshly prepared malt extract acting at 65° for 90 minutes produced 82.7% of maltose.

Microscopic Appearance of Starch. When examined microscopically, starch granules appear to be made up of a series of distinctly stratified concentric or eccentric layers, the outer ones being usually wider and denser than those nearer the center or hilum, the latter appearing as a dark spot. Often two or more nuclei appear in the same granule, being usually each surrounded with concentric circles. In all starch granules, the outer layer is of oldest growth, the granule increasing in size from without inwards. For this reason the successive layers as the center is approached are softer and less compact. Inasmuch as these layers vary greatly in thickness, the individual granule gradually changes from the original spherical to an oval or ovoid form.

A. Schimper[1] finds that inasmuch as the shape and size of the starch grains in plants depends to a large extent on their situation in the chlorophyl cells, it follows that if the latter are of well arranged form, the starch granules are disengaged freely and attain regular forms and normal size, while if the former are misshapen the latter have not the freedom of movement and are smaller. He considers starch grains as consisting of radial crystalline aggregates (sphaerocrystals), differing, however, from ordinary crystals by their power of swelling, and are more properly termed crystalloids—occurring in aggregates only.

Chemical Properties of Starch. Starch (when the granules

---

[1] Bot. Ztg. 1880, 881; 1881, 185; 1883, Nos. 7–10; 1885, 738; Bied. Centr. 1881, 479; J. C. S. 1881, **40**, 1061; Ann. Sci. nat. 1880–1881, **11**, 256, 265; abst. Quart. J. Micro. Sci. 1881, **21**, 291.

are unbroken) is absolutely insoluble in cold water,[1] alcohol, ether, chloroform or other solvent. Air-dried starch usually contains about 18% of moisture, but this amount may vary within quite wide limits, depending upon the hygrometric state of the atmosphere. According to F. Ullik,[2] starch has a great affinity for water, which varies according to the nature of the starch. Potato starch which, when dried at 120° was found to contain 12.1% water, was weighed out in amounts corresponding to 20 gm. of the air-dry substance, and mixed with an equal weight of water, when the following increments in temperature were observed:

	Increase in Temperature.
1. Anhydrous starch (dried at 120°)	13.8°
2. Starch dried at 90°	12.0°
3. Starch dried over conc. sulfuric acid	8.8°
4. Air dried starch	3.0°

The gain of water which these samples showed were: (2) 0.85%, (3) 2.6%, (4) 12.1%. He also has established that starch which has been exposed in an atmosphere saturated with moisture at a temperature of 16°–20° contains about 37% water, and that no rise in temperature on mixing with water occurs. The moisture in starch may be determined by means of organo-magnesium compounds, especially magnesium methyl iodide as first suggested by H. Hibbert and J. Sudborough,[3] and extended by T. Zerewitinoff.[4]

The moisture present in starch may be entirely driven off by exposure in a current of dry air at a temperature of 105°, in

---

[1] W. Wicke, Pogg. Ann. 1859, **108**, 359; abst. Rep. Chim. Pure, 1860, **2**, 42; Jahr. Chem. 1859, **12**, 544.

[2] Zts. f. d. gesammt. Brauw. 1891, 565; abst. J. S. C. I. 1893, **12**, 281; J. C. S. 1892, **62**, 1066; Chem. Centr. 1892, **63**, I, 250, 432; Dingl. Poly. 1892, **285**, 184, 211; Jahr. Chem. 1892, **45**, 2820.

[3] J. C. S. 1904, **85**, 933; abst. Chem. News, 1904, **89**, 19; J. S. C. I. 1904, **23**, 77; Rep. Chim. 1904, **4**, 144; Chem. Centr. 1904, **75**, I, 402; Jahr. Chem. 1904, **57**, 817.

[4] Ber. 1907, **40**, 2123; 1908, **41**, 2233; 1910, **43**, 3590; Zts. anal. Chem. 1911, **50**, 680; abst. J. S. C. I. 1907, **26**, 646; 1908, **27**, 839; 1911, **30**, 107, 1233; C. A. 1908, **2**, 2810; 1911, **5**, 1285; 1913, **7**, 2390; J. C. S. 1907, **92**, ii, 509; 1908, **94**, i, 593; 1911, **100**, i, 101; 1912, **102**, ii, 1026; Chem. Zentr. 1907, **78**, II, 97; 1908, **79**, II, 445; 1912, **83**, II, 1401.

which condition it is very hygroscopic[1] in a moist atmosphere.

The specific gravity of air-dried starches vary within comparatively wide limits, due primarily to the varying amounts of moisture contained therein. Anhydrous starches, however, have not identical gravities, anhydrous potato having a gravity of 1.65 and anhydrous arrowroot, 1.565.

In determining the action of ultra-violet rays upon starch, L. Massol[2] exposed solutions of starch of 0.2%–1.0% concentration at 10 cm. distance to the action of a mercury vapor quartz lamp. The starch gradually lost the property of giving a blue solution with iodine. It is to be noted that the rate of transformation increases on decreasing the concentration and acidifying medium. As the result of the exposure the solutions acquire reducing power, and the starch is less precipitable with alcohol. It appears the reducing substances formed consist of, or contain maltose. According to others,[3] the treated solution acquires an acid reaction, and contains dextrins, dextrose, pentoses and formaldehyde.

When starch solutions are exposed for some hours to X-rays of moderate penetrating power,[4] the opacity and viscosity of the solutions are markedly diminished, and there is a partial conversion to soluble starch and dextrin. Dextrin under similar conditions is not convertible into dextrose. The effect is attributed to a direct action upon the starch molecule, either by the X-rays or by the secondary rays which they produce. In investigating the electric transport of starch, W. Hardy[5] and F. Bottazzi[6] are

[1] W. Nossian, J. prakt. Chem. 1861, **83,** 42; abst. J. Pharm. Chim. 1861, **40,** 158; Chem. Centr. 1861, **32,** 815; Jahr. Chem. 1861, **14,** 714; Wag. Jahr. 1861, **7,** 359.

[2] Compt. rend. 1911, **152,** 902; 1912, **154,** 1645; abst. J. C. S. 1911, **100,** i, 356; 1912, **102,** i, 538; J. S. C. I. 1911, **30,** 503; C. A. 1911, **5,** 2095; 1912, **6,** 2421; 1913, **7,** 430; Chem. Zentr. 1911, **82,** I, 1686; Chem. Ztg. 1911, **35,** 453; Meyer Jahr. Chem. 1911, **21,** 528; Wag. Jahr. 1911, **57,** II, 310.

[3] J. Bielecki and R. Wurmser, Compt. rend. 1912, **154,** 1429; abst. J. C. S. 1912, **102,** i, 538; J. S. C. I. 1912; **31,** 599; C. A. 1912, **6,** 2082, 2916; Biochem. Zts. 1912, **43,** 154; Chem. Zentr. 1912, **83,** II, 243, 1274; Meyer Jahr. Chem. 1912, **22,** 431.

[4] H. Colwell and S. Russ, Proc. Phys. Soc. 1912, **24,** 214; Le Radium, 1912, **9,** 230; J. C. S. 1912, **102,** i, 608; C. A. 1912, **6,** 2863; Chem. Zentr. 1912, **83,** II, 705.

[5] J. physiol. 1905, **33,** 251; abst. J. C. S. 1906, **90,** i, 121; Biochem. Centr. 1906–1907, **5,** 41; Chem. Centr. 1906, **77,** I, 688; Jahr. Chem. 1905–1908, II, 4528.

[6] Atti. R. Acad. Lincei, 1909, **18,** ii, 87; abst. J. C. S. 1909, **96,** i, 700; C. A. 1910, **4,** 342; Chem. Zentr. 1909, **80,** II, 167; Jahr. Chem. 1909, **63,** II, 379.

not in accord. According to the former, glycogen and starch are relatively isoelectric hydrosols. When solutions of glycogen and starch are subjected to a field of about 5 volts per cm. (0.1 milliampere), both move toward the anode, only traces migrating toward the cathode. In the presence of small proportions of mineral acid, alkalis or salts, starch behaves like protein or gelatin in acid solution in that it migrates towards the cathode, and in alkaline solution towards the anode. In the presence of neutral salts no migration is observed. W. Loeb[1] claims the effect of the silent electric discharge on starch solution is to produce hydrolysis. W. Baily[2] has studied the optical properties of starch, while W. Hartley[3] has investigated the absorption spectrum.

Anhydrous starch has been prepared by the distillation of ordinary starch with a mixture of anhydrous benzene and absolute alcohol, using Young's method of fractionation.[4] Dehydration is complete when the boiling point of the alcohol-benzene binary mixture (68.25°) becomes constant.

F. Sestini claims[5] that when bread crust is heated in a tube, furfural begins to form at 110°–115°, whereas if heated in the open, furfural formation does not commence until 150° is reached. Gridkoff was unable to detect furfural by the distillation of cellulose with dilute sulfuric acid, but when starch is heated dry at about 200° or in the presence of acid at about 100°, a noticeable yield of furfural results. When heated with aniline, only dextrin is formed,[6] while glycerol does not attack starch even at 200°. C. Husson[7] unsuccessfully endeavored to synthesize albumin by

[1] Biochem. Zts. 1912, **46**, 121; 1914, **60**, 286; abst. C. A. 1913, **7**, 476; 1914, **8**, 1746; J. C. S. 1912, **102**, i, 947; 1914, **106**, i, 500; Bull. Soc. Chim. 1913, **14**, 1076; Chem. Zentr. 1912, **83**, II, 2063.

[2] Phil. Mag. 1876, (5), **2**, 123; abst. J. C. S. 1877, **31**, 294; Jahr. Chem. 1876, **29**, 147.

[3] J. C. S. 1887, **51**, 59; abst. Chem. News, 1886, **54**, 270; J. S. C. I. 1887, **6**, 285; J. pharm. chim. 1888, **50**, 120, 524; Ber. 1887, **20**, R, 174; Jahr. Chem. 1887, **40**, 350.

[4] W. Atkins and E. Wilson, J. C. S. 1915, **107**, 916; abst. J. S. C. I. 1915, **34**, 818; C. A. 1915, **9**, 2473; Zts. ang. Chem. 1915, **28**, II, 618.

[5] L'Orosi, 1898, **21**, 109; Chem. Centr. 1898, II, 182; J. S. C. I. 1898, **17**, 861; J. C. S. 1899, **76**, i, 103; Jahr. Chem. 1898, **51**, 2265.

[6] H. Schiff, Ber. 1871, **4**, 908; abst. J. C. S. 1872, **25**, 150; Chem. News, 1871, **24**, 300; Jahr. Chem. 1871, **24**, 798; Zts. Chem. 1871, **14**, 725.

[7] Compt. rend. 1872, **75**, 549; abst. J. C. S. 1873, **26**, 46; Bull. Soc. Chim. 1872, **18**, 453; Ber. 1872, **5**, 830.

the action of nitrogen iodide on starch. R. Rother[1] has studied the influence of starch on the solubility of albumen.

Various starches have been found to vary as to their gelatinizing temperatures. According to M. Nyman,[2] when rye starch is mixed with water and gradually heated, it gelatinizes at 57°; barley at 58°, and wheat starch at 59°. The gelatinizing point was taken as being the temperature at which the starch grains ceased to polarize light when examined under the micropolariscope. Working with a slight modification of the method of Francis and Smith,[3] the gelatinization temperature of corn starch was found to vary between 64.1°–71.1°, although concordant results were readily obtained for a given variety.[4]

It has been found[5] that potato starch contains 0.06% of chemically combined phosphorus which can not be removed by extraction with dilute acid, either as free or combined phosphoric acid. The analyses of phosphorous content in starch as made by A. Thomas[6] is considered to support the view that it is in chemical combination.

A. Rakovski,[7] has contributed a series of papers on the absorption of salts dissolved in water by starch, including NaOH,[8]

---

[1] Pharm. J. Trans. 1873, (3), **3**, 644; abst. J. C. S. 1873, **26**, 919; Jahr. Chem. 1873, **26**, 828.

[2] Zts. Nahr. Genussm. 1912, **24**, 673; abst. J. C. S. 1913, **104**, ii, 160; J. S. C. I. 1913, **32**, 40; C. A. 1913, **7**, 665.

[3] J. Ind. Eng. Chem. 1916, **8**, 509; abst. C. A. 1916, **10**, 2995; J. S. C. I. 1916, **35**, 750.

[4] A. Dox and G. Roark, J. A. C. S. 1917, **39**, 742; abst. J. C. S. 1917, **111**, ii, 276; C. A. 1917, **11**, 1763; J. S. C. I. 1917, **36**, 560.

[5] J. Northrup and J. Nelson, J. A. C. S. 1916, **38**, 472; abst. J. C. S. 1916, **109**, i, 373; C. A. 1916, **10**, 766.

[6] Biochem. Bull. 1914, **3**, 403; abst. J. C. S. 1915, **108**, ii, 6; C. A. 1914, **8**, 3801. According to A. Fernbach (Compt. rend. 1904, **138**, 428; abst. J. C. S. 1904, **86**, i, 294; J. S. C. I. 1904, **23**, 330; Chem. Centr. 1904; **75**, I, 819; Jahr. Chem. 1904, **57**, 1150) when potato starch is levigated, two kinds of granules—the heavy and the light—are obtained. Both contain phosphorus, a higher percentage in the light granules (0.158–0.226% P_2O_5) as against 0.138–0.178% in the heavy granules.

[7] J. Russ. Phys. Chem. Soc. 1911, **43**, 170; 1912, **44**, 586, 1722; 1913, **45**, 13; abst. J. C. S. 1911, **100**, ii, 470; 1912, **102**, ii, 743; 1913, **104**, ii, 114, 303; C. A. 1912, **6**, 2348, 2876; 1913, **7**, 1121, 2144, 2880; Chem. Zentr. 1911, **82**, I, 1478, 1479; 1912, **83**, I, 568; II, 667; 1913, **84**, I, 586, 1384, 1806.

[8] A. Rakovski, J. Russ. Phys. Chem. Soc. 1913, **45**, 7; Zts. Chem. Ind. Koll. 1913, **12**, 128; abst. J. S. C. I. 1913, **32**, 440; C. A. 1913, **6**, 2876; 1914, **7**, 2880; J. C. S. 1913, **102**, ii, 302; Bull. Soc. Chim. 1913, **14**, 787; Chem. Zentr. 1913, **84**, I, 1384, 1806.

ammonia,[1] and cupric hydroxide.[2] It has been found that the absorption of sodium hydroxide from aqueous solutions by potato starch is increased by the presence of sodium or potassium salts of organic or inorganic acids, the effect being greater the higher the concentration of the salt. Slight absorption of ammonia from aqueous solutions by starch is practically unaffected by the presence of ammonium chloride. Whereas strongly dissociated alkalis are absorbed in considerable proportions, the feebly dissociated ammonia is slight, and falls virtually to zero in the presence of the strongly dissociated barium hydroxide. The heats of combustion per gm./mol. for constant volume and constant pressure are: for cellulose, 678; starch, 677.5. The heats of formation are 231.0 and 231.5 respectively.[3]

It has been shown[4] that a solution of potato starch frozen to a solid mass and then melted, yields a coagulum nearly free from mineral matter. In fact, the starch may be completely "demineralized"[5] by heating a 1% paste in an autoclave for 2–3 hours at 130°, cooling, decanting the supernatant opalescent liquid from a slight sandy residue, and then freezing in a mould of pure nickel. On melting the solid block of ice, the flocculent residue was found to contain less than 0.02% of ash. They have found[6] that starch desiccated by drying in vacuo over phosphorus pentoxide, becomes soluble in cold water through the formation of dextrins. When desiccation has been carried so far that not

---

[1] A. Rakovski, J. Russ. Phys. Chem. Soc. 1911, **44**, 586; Zts. Chem. Ind. Koll. 1912, **11**, 51; abst. J. S. C. I. 1912, **31**, 891; C. A. 1912, **6**, 2348; J. C. S. 1912, **102**, ii, 743; Bull. Soc. Chim. 1912, **12**, 1411; Chem. Zentr. 1912, **83**, II, 668.

[2] A. Rakovski, J. Russ. Phys. Chem. Soc. 1914, **46**, 246; abst. J. C. S. 1914, **106**, ii, 434; C. A. 1914, **8**, 2512; Bull. Soc. Chim. 1914, **16**, 868.

[3] F. Stohmann and H. Langbein, J. prakt. Chem. 1891, **152**, 336; 1892, **153**, 305; abst. J. C. S. 1892, **62**, 4, 764; Chem. News, 1894, **70**, 121, 294; J. S. C. I. 1891, **10**, 1020; Bull. Soc. Chim. 1892, **8**, 303; Ber. 1891, **24**, R, 881; 1892, **25**, R, 126, 496; Jahr. Chem. 1892, **45**, 369, 373.

[4] G. Malfitano and A. Moschkoff, Compt. rend. 1910, **150**, 710; abst. J. S. C. I. 1910, **29**, 506; J. C. S. 1910, **98**, i, 301; C. A. 1910, **4**, 1556; Chem. Zentr. 1910, **81**, I, 2074; Jahr. Chem. 1910, **63**, II, 408.

[5] G. Malfitano and A. Moschkoff, Compt. rend. 1910, **151**, 817; abst. J. S. C. I. 1910, **29**, 1402; J. C. S. 1910, **98**, i, 817; C. A. 1911, **5**, 1345; Chem. Zentr. 1911, **82**, I, 17; Jahr. Chem. 1910, **63**, II, 407; Wag. Jahr. 1910, **56**, II, 257. See also G. Malfitano, Compt. rend. 1904, **139**, 1221; 1906, **143**, 400; Rev. gén. sci. 1908, **19**, 614; J. C. S. 1906, **90**, i, 804; Chem. Centr. 1906, **77**, II, 1312; Jahr. Chem. 1905–1908, II, 939.

[6] G. Malfitano and A. Moschkoff, Compt. rend. 1912, **154**, 443; abst. J. S. C. I. 1912, **31**, 245; J. C. S. 1912, **102**, i, 240; C. A. 1912, **6**, 1552; Bull. Soc. Chim. 1912, **11**, 773; Chem. Zentr. 1912, **83**, I, 1103.

only water of hydration is evolved, but also water of constitution proceeding from the decomposition of the molecule, then the solubility diminishes. So-called "crystals" of starch, when examined microscopically,[1] although resembling crystals of dextrose, are not crystalline in form. These particles of starch have not the polyhedric form, neither do they exhibit the phenomena of birefringence.[2]

Many of the starches exhibit well marked acidic properties, especially rice starch. When the latter[3] is allowed to remain in contact with sodium, potassium or barium hydroxides, it is found that there is a considerable diminution of the titer of the alkali—less so with ammonia. The absorbed alkali can again be extracted with water. The diminution of the alkali titer is accompanied by the formation of an equivalent quantity of sodium hydrogen carbonate. Potassium and sodium chlorides, sulfates and phosphates are all absorbed by starch. More copper acetate than sulfate is absorbed. Zinc and copper are taken up from ammoniacal solutions of the sulfates, the copper product being relatively stable, water extracting ammonia but no appreciable amount of copper from it.[4]

J. Groll[5] has found that reversible transformations of starch into erythroamylose may take place, giving a red or violet color with I-KI solution, when the starch solution is treated with methyl, ethyl or octyl alcohols, ethyl ether or chloroform, in various concentrations. If sodium cholate or saponin is added to these solutions, transformation into erythroamylose becomes irreversible, this being ascribed to a surface tension effect.

As the result of dialyzing solutions of soluble starch, precip-

---

1. Bull. Soc. Chim. 1912, (4), **11**, 606; Compt. rend. 1913, **156**, 1412; abst. J. C. S. 1912, **102**, i, 608; 1913, **104**, i, 593; J. S. C. I. 1913, **32**, 619; C. A. 1912, **6**, 2875.
2. G. Malfitano and A. Moschkoff, Compt. rend. 1913, **156**, 1681; abst. J. C. S. 1913, **104**, i, 707; C. A. 1913, **7**, 2937; Chem. Zentr. 1913, **84**, II, 492, 493.
3. E. Demoussy, Compt. rend. 1906, **142**, 933; abst. J. C. S. 1906, **90**, i, 401; J. S. C. I. 1906, **25**, 489; Rep. Chim. 1906, **6**, 312; Chem. Centr. 1906, **77**, I, 1654; Jahr. Chem. 1905–1908, II, 933. See J. Ford and J. Guthrie, J. C. S. 1906, **89**, 76; abst. J. S. C. I. 1906, **25**, 228; Bull. Soc. Chim. 1906, **36**, 1293; Chem. Centr. 1906, **77**, I, 314, 990; Jahr. Chem. 1905–1908, II, 923; Chem. News, 1905, **92**, 1293.
4. W. Bate, E. P. 23703, 1903; abst. J. S. C. I. 1904, **23**, 944.
5. Arch. neerland. physiol. 1918, **2**, 319; abst. J. C. S. 1918, **114**, i, 292; C. A. 1918, **12**, 485; J. S. C. I. 1918, **37**, 134-A.

itating the solution left in the dialyzer by alcohol and a trace of NaCl, E. Clark[1] concludes that soluble starch carries associated with it certain amounts of dextrins with reducing properties, and that it can only be freed from these by dialysis or precipitation. A. Fernbach prepares a pure soluble starch by slowly pouring weak aqueous solutions of starch (2%) into a large excess of pure acetone, the flocculent precipitate after exhausting with acetone, being dried at low temperature in a vacuum. This starch is completely soluble in cold water, its solution giving a very pure blue color with iodine.[2]

In investigating the colloidal properties of starch in reference to its constitution, E. Fouard[3] has observed that in preparing a collodion-dialyzed starch solution as previously indicated, the rotatory power diminishes, at first rapidly, then more slowly, and finally approaches asymptotically to the rotatory power for a maltose solution, the change being reversable, so that the rotation again increases on neutralization. From this the inference is drawn that starch is simply a condensation of maltose of varying degrees of complexity.[4] The production of lactic acid from starch[5] is a well-known industry.[6]

L. Maquenne has shown that starch paste slowly reverts to amylocellulose,[7] but this action has been shown to be reversible between the temperatures of 0°–150°.[8] At higher temperatures

---

[1] J. Biol. Chem. 1910, **7**, 45; abst. J. C. S. 1910, **98**, i, 544. Biochem. Bull. **1**, 194; abst. C. A. 1912, **6**, 1161.

[2] Eighth Intl. Cong. Appl. Chem. 1912, **13**, 131; Compt. rend. 1912, **155**, 617; abst. J. C. S. 1912, **102**, i, 832; J. S. C. I. 1912, **31**, 892; C. A. 1912, **6**, 3339; Bull. Soc. Chim. 1913, **13**, 86; Chem. Zentr. 1912, **83**, II, 1812; Meyer Jahr. Chem. 1912, **22**, 429.

[3] Compt. rend. 1907, **144**, 501, 1366; 1908, **146**, 285, 978; 1908, **147**, 813, 931; 1909, **148**, 502; abst. J. S. C. I. 1907, **26**, 832; J. C. S. 1907, **92**, i, 391; 1908, **94**, i, 138, 503, 953; 1909, **96**, i, 13, 209.

[4] A. Claflin, J. S. C. I. 1897, **16**, 516; abst. J. C. S. 1899, **76**, i, 12; Chem. Centr. 1897, **68**, II, 338; Jahr. Chem. 1897, **50**, 1223.

[5] W. McLauchlan, Seventh Intl. Cong. Appl. Chem. 1909; abst. J. S. C. I. 1909, **28**, 734.

[6] W. Hoffmann, Zts. Spiritusind. 1913, **36**, 71; abst. J. S. C. I. 1913, **32**, 303; Deut. Essigind. 1913, **17**, 102; C. A. 1913, **7**, 2647; Chem. Zentr. 1913, **84**, I, 1311; Zts. ang. Chem. 1913, **26**, II, 371; Wag. Jahr. 1913, **59**, II, 363.

[7] Compt. rend. 1903, **137**, 88, 658, 797, 1266; abst. J. C. S. 1903, **84**, i, 679; 1904, **86**, i, 17, 227, 228, 294, 800; Bull. Soc. Chim. 1903, **29**, 218; Rep. Chim. 1904, **4**, 102, 177; Chem. Centr. 1903, **74**, II, 757; Jahr. Chem. 1903, **56**, 1005.

[8] Compt. rend. 1904, **138**, 1356; 1905, **140**, 440, 943, 1259; 1906, **142**, 95; abst. J. C. S. 1904, **86**, ii, 625; 1905, **88**, 262, 328, 624; J. C. S. 1906, **90**, i, 235; J. S. C. I. 1904, **23**, 675; 1905, **24**, 285, 507, 630; 1906, **25**, 130.

the amylocellulose liquefies and on cooling forms a starch paste which is colored blue by iodine. The statement of Naegeli that the skeleton-like substance obtained from starch by treatment with dilute acid is amylodextrose has been corroborated by Griessmayer.[1]

In 1856 H. v. Payr observed[2] the action of tin chloride upon starch. When chloroform is added to a solution of starch in tin chloride and allowed to remain at rest for several months, the starch is wholly converted into dextrin. When starch paste is treated with chloroform a soluble modification is formed, similar to that resulting from treatment with mineral acids as HCl, and upon heating such a mixture, the starch after some time passes entirely into solution, which upon cooling, separates as a fine precipitate.

When starch is shaken with 100 times its weight of 15% aqueous chloral hydrate an almost clear but viscous solution results, which is not colored blue with elemental iodine or an iodine solution in chloral hydrate.

Tannin immediately induces precipitation from starch paste or from soluble starch, the product being soluble in boiling water, from which it is again deposited upon cooling.

The sp. gr. of potato starch will average 1.60[3] to 1.65;[4] wheat starch, 1.643,[5] and air-dried starch 1.53–1.54.[6]

Starch Paste. This may readily be prepared by the methods

---

[1] V. Griessmayer, Allgem. Brauer. u. Hopfenztg, **26**, 147; abst. J. S. C. I. 1887, **6**, 446; Bied. Centr. 1887, **16**, 190; J. C. S. 1887, **52**, 686.

[2] J. prakt. Chem. 1856, **69**, 425; Sitzber. k. k. Akad. Wiss. **21**, 269; abst. J. pharm. chim. 1857, **31**, 318; Chem. Centr. 1856, **27**, 858; Jahr. Chem. 1856, **9**, 672.

[3] O. Saare, Zts. Spiritusind. **7**, 550; abst. Chem. News, 1885, **51**, 297; J. C. S. 1885, **48**, 618; Chem. Tech. Rep. 1884, **23**, I, 251; Chem. Ztg. 1884, **8**, 934; Jahr. Chem. 1884, **37**, 1654.

[4] H. Rodewald, Landw. Versstat. 1894, **45**, 201; abst. J. C. S. 1895, **68**, i, 165; Chem. Centr. 1895, **66**, I, 76; Jahr. Chem. 1894, **47**, 1137.

[5] H. Rodewald and A. Kattein, Zts. physik. Chem. 1900, **33**, 590; abst. J. C. S. 1900, **78**, i, 79, 477; J. S. C. I. 1899, **28**, 1062; Chem. Centr. 1899, **70**, II, 419; 1900, **71**, II, 180; Jahr. Chem. 1899, **52**, 1271; 1900, **53**, 829.

[6] E. Parrow, Ellrodt and F. Neumann, Zts. Spiritusind. 1907, **30**, 432; abst. J. S. C. I. 1907, **26**, 1103; Chem. Zentr. 1907, **78**, II, 1606; Jahr. Chem. 1905–1908, II, 932; Wag. Jahr. 1907, **53**, II, 217. For bleaching of starch, see A. Holste, E. P. 30390, 1909; abst. J. S. C. I. 1910, **29**, 1200. For action of glycerol on starch, see K. Zulkowsky, Ber. 1880, **13**, 1395; abst. J. C. S. 1880, **38**, 865; Monatsh. 1905, **26**, 1420; Akad. Wien. 1880, **72**, II Abth. 384. K. Zulkowsky and B. Franz, Ber. Oesterr. Gess. zur Foerderung. Chem. Ind. 1894, **16**, 120.

of C. Higgins,[1] C. Ekman,[2] or G. Gastine.[3] In the former, starch is digested with water and a digesting agent at a temperature just below its gelatinizing point, until it is converted into white dextrin as indicated by a violet reaction with iodine. The temperature is raised and the mass kept liquid for a short time, after which it is neutralized with alkali and allowed to cool to a soft semi-fluid mass. In the second method, rice starch is heated with dilute mineral acid at a temperature not exceeding 35°, and then neutralized with a base as calcium carbonate or magnesium oxide. In the Gastine process, potato starch is heated with a trace of mercuric iodide, stirred, poured into boiling water, allowed to settle and the supernatant liquid used. The keeping properties of the paste may be increased by the addition of a drop of mustard oil,[4] a trace of mercuric chloride,[5] or a small amount of alkali, as sodium hydroxide.[6] The amount of alkali to be added is insufficient to have any influence when the starch solution is used as an indicator in iodometric titration, yet effectually prevents bacterial decomposition of the starch solution.

In determinations requiring the use of a very delicate iodine solution—such as the estimation of sulfurous acid in wines—the end-point of the titration is often not clear cut when using ordinary starch paste. According to L. Mathieu,[7] the soluble starch described by A. Fernbach and J. Wolff,[8] affords greater precision in titration than any other. In the preparation of this

---

1. E. P. 19021, 1898; 1885, 1900; abst. J. S. C. I. 1899, **18**, 59. U. S. P. 642330, 1900. Rev. Prod. Chim. **16**, 244; abst. J. S. C. I. 1900, **19**, 1126.

2. U. S. P. 742174, 1903; abst. J. S. C. I. 1903, **22**, 1252; Mon. Sci. 1904, **61**, 38. E. P. 8331, 1901; abst. J. S. C. I. 1902, **21**, 358; Chem. Ztg. 1902, **26**, 811. See M. Brauer, D. R. P. 262501, 273311; abst. J. S. C. I. 1914, **33**, 747.

3. Bull. Soc. Chim., 1888, **50**, 172; abst. J. C. S. 1889, **56**, 73; Chem. News, 1888, **58**, 245; Ber. 1888, **21**, R, 802; Chem. Centr. 1888, **59**, 1240; Chem. Ind. 1888, **11**, 561; Chem. Tech. Rep. 1888, **27**, II, 265; Jahr. Chem. 1888, **41**, 2519; Zts. anal. Chem. 1889, **28**, 339.

4. A. Hirschberg, Arch. Pharm. (2), **150**, 44; abst. Chem. Centr. 1872, **43**, 492; J. C. S. 1873, **26**, 100; Jahr. Chem. 1872, **25**, 782.

5. R. Lansdale, E. P. 1803, 1875.

6. Pollitz, Zts. ang. Chem. 1917, **30**, I, 132; abst. J. C. S. 1917, **112**, ii, 499; C. A. 1918, **12**, 666.

7. Ann. Chim. Analyt. 1911, **16**, 51; abst. J. S. C. I. 1911, **30**, 399. Bull. Assoc. chim. Sucr. Dist. 1910, **27**, 1166; abst. J. C. S. 1910, **96**, ii, 747; C. A. 1910, **4**, 2617; Chem. Zentr. 1910, **81**, II, 685; Jahr. Chem. 1910, **63**, I, 496.

8. Compt. rend. 1907, **144**, 645; J. C. S. 1907, **92**, i, 750, 1012; J. S. C. I. 1907, **26**, 833, 938; Rep. Chim. 1908, **8**, 61, 89; Chem. Zentr. 1907, **78**, I, 1339; Jahr. Chem. 1905–1908, II, 924, 938, 943.

material, starch is allowed to remain in contact with dilute HCl (1:1000) for some time, then washed with distilled water and dried at 30°, followed by several hours' heating in an oven at or above 100°. The acid treatment removes alkalis and alkaline earths and converts neutral into acid phosphates, while during the subsequent dry heating, gradual conversion into soluble starch takes place. It is said that this material keeps indefinitely in the dry state, and is converted into paste by boiling in 100 volumes of distilled water and filtering the solution thus obtained. It is said that this solution is very sensitive to iodine, giving a sharp change from colorless to pure blue, and conversely. These investigators state[1] that when starch paste is made neutral to methyl orange by the addition of sulfuric acid and then heated at 120°, its viscosity is greatly diminished, but if disodium hydrogen phosphate be added to the neutralized paste directly before heating, the viscosity is increased and becomes equal to that of the original paste, when the quantity of the salt added is equivalent to 2.5 times that of the equivalent of the acid. The effect of sodium hydroxide in retarding the liquefaction of starch paste is much more marked than that of Na_2HPO_4. It appears therefore, that the liquefaction of neutralized starch paste is partly due to the transformation of the secondary phosphates present in the starch into primary phosphates; that it is not affected by the addition of salts neutral to methyl orange, but is retarded by the addition of salts alkaline to this reagent, and checked altogether by traces of free alkali.

A. Fernbach and J. Wolff have also shown[2] that when 5%

[1] A. Fernbach and J. Wolff, Compt. rend. 1906, **143**, 380; abst. J. C. S. 1906, **90**, i, 804; Ann. Brass. 1906, 361; J. S. C. I. 1906, **25**, 898; Chem. Centr. 1906, **77**, II, 1046; Jahr. Chem. 1905–1908, II, 4786. See also Compt. rend. 1906, **143**, 380; 1907, **145**, 261; abst. J. S. C. I. 1907, **26**, 938. J. Wolff and A. Fernbach, Compt. rend. 1903, **22**, 1302; Bull. Soc. Chim. 1904, **31**, 766; Chem. Centr. 193, **74**, II, 1451; Jahr. Chem. 1903, **56**, 1912.

[2] A. Fernbach, Woch. Brau. 1900, **17**, 24; Ann. Brass. 1899; abst. J. S. C. I. 1900, **19**, 260; Compt. rend. 1904, **138**, 428; J. S. C. I. 1904, **23**, 330; Compt. rend. 1906, **142**, 285; Zts. Bierbr. 1906, 349; Ann. Brass. 1906, 12; Woch. Brau. 1906, **23**, 159, 160; abst. J. C. S. 1906, **90**, i, 3271; J. S. C. I. 1906, **25**, 192; Rep. Chim. 1906, **6**, 187; Chem. Zts. 1907, **6**, 40, 266; Jahr. Chem. 1905–1908, II, 4670; Wag. Jahr. 1906, **52**, II, 339, 350. Eighth Intl. Cong. Appl. Chem. 1912, VI^a, 592; abst. J. S. C. I. 1912, **31**, 892. A. Fernbach and M. Schön, Bull. Soc. Chim. 1912, **11**, 303; abst. J. S. C. I. 1912, **31**, 402. A. Fernbach and J. Wolff, J. Fed. Inst. Brew. 1904, **10**, 216; abst. J. S. C. I. 1910, **29**, 616; Seventh Intl. Cong. Appl. Chem. 1907; abst. J. S. C. I. 1909, **28**, 847; Compt. rend. 1907, **145**, 80; abst. J. S. C. I. 1907, **26**, 833; Compt. rend. 1903, **137**, 718; Bull. Soc. Chim. 1904, **31**, 766; abst. Chem.

starch paste is treated with a few drops of neutral H_2O_2 and ammonia and placed at a temperature of 70°–75°, rapid liquefaction occurs, the liquid attaining the viscosity of water in about 15 minutes. Ferrous sulfate or copper sulfate also attenuate the viscosity, but a longer time is required.

As M. Samec alone,[1] and with S. Jencic,[2] and F. v. Hoefft,[3] have shown, aging or retrogression of a starch solution is accompanied by a well-marked irreversible diminution in viscosity; the final viscosity of a 1% solution being of the order of that of molecular-disperse (true) solutions; electric conductivity of the solution increases; the addition of HCl reduces the initial viscosity of the solution and retards the subsequent decrease in viscosity; the stabilizing action varies according to the concentration of the acid.

From a comparison of the behavior of ordinary and phosphorus-free starches,[4] it would appear that initial changes produced by alkalis as seen in the starch solutions, are—at least in great measure—due to the action of the alkali upon the phosphoric acid groups in the starch molecule. Further action results in the combination of the alkali with other groups in the starch molecule, and in the peptonization of the starch. It is claimed[5] that by the action of 0.125 N potassium hydroxide, it is possible to separate starch into two fractions, one of which does, and the

---

Centr. 1903, **74**, II, 1457; Jahr. Chem. 1903, **56**, 1912; Compt. rend. 1905, **140**, 95; abst. J. S. C. I. 1905, **24**, 144. Compt. rend. 1905, **140**, 1067, 1403; abst. J. S. C. I. 1905, **24**, 508.

[1] Kolloidchem. Beihefte, 1912, **4**, 132; abst. J. S. C. I. 1913, **32**, 102; C. A. 1913, **7**, 3767; J. C. S. 1913, **104**, i, 17; Chem. Zentr. 1913, **84**, I, 632; Meyer Jahr. Chem. 1912, **22**, 430.

[2] Koll. Chem. Beihefte. 1915, **7**, 137; abst. J. C. S. 1915, **108**, i, 941; J. S. C. I. 1915, **34**, 1264; C. A. 1916, **10**, 289. See also G. Malfitano and A. Moschkoff, Compt. rend. 1910, **150**, 710; **151**, 817; abst. J. C. S. 1910, **98**, i, 301, 817; C. A. 1911, **5**, 1345; J. S. C. I. 1910, **29**, 1402; Chem. Zentr. 1911, **82**, I, 17; Jahr. Chem. 1910, **63**, II, 407; Wag. Jahr. 1910, **56**, II, 257.

[3] Koll. Chem. Beihefte, 1913, **5**, 141; abst. J. S. C. I. 1913, **32**, 954; C. A. 1914, **8**, 837, 1602; J. C. S. 1913, **104**, i, 1155. See also C. Tanret, Compt. rend. 1909, **148**, 1775; abst. C. A. 1909, **3**, 2676; J. C. S. 1909, **96**, i, 556; J. S. C. I. 1909, **28**, 847; Bull. Soc. Chim. 1909, **5**, 310, 823; Rep. Chim. 1910, **10**, 66; Chem. Ztg. 1909, **33**, 837; Jahr. Chem. 1909, **62**, II, 374; Wag. Jahr. 1909, **55**, II, 226.

[4] M. Samec, Koll. Chem. Beihefte, 1916, **8**, 33; abst. J. C. S. 1916, **109**, i, 308; C. A. 1917, **11**, 312.

[5] M. Samec, Koll. Chem. Beihefte, 1911, **3**, 123; 1912, **4**, 132; 1914, **6**, 23; Intern. Zts. Phys.-chem. Biol. 1914, **1**, 173; abst. J. C. S. 1912, **102**, ii, 144; 1913, **104**, i, 17, 1155; 1914, **166**, i, 930; J. S. C. I. 1914, **33**, 760.

other does not contain phosphoric acid, either free or combined.

The properties of "demineralized" starch prepared by the methods of Wolff and Fernbach,[1] and G. Malfitano and A. Moschkoff,[2] correspond to a solution of ordinary aged starch as described above, there being many facts known in strong confirmation of the view that the characteristic properties of starch as exemplified in starch paste are due to the presence of amlophosphoric acid or analogous complex compound,[3] probably of the type $R.CH_2O.$-$PO(OH)_2$. As a generality, the formation of soluble starch is accompanied by a reduction in size of the starch molecule.[4]

As F. Schardinger has shown,[5] specific microbes act upon starch paste with the production of soluble substances similar to dextrin. The action of the same organism (*Bac. macerans*) under identical conditions, differs according to the kind of starch used, potato being entirely, arrowroot largely, and wheat and rice starch difficultly dissolved.

Processes for the coloring[6] and perfuming[7] of starch pastes for selective purposes have been patented.

The value of a starch paste from a technical point of view, rests upon a determination of the gelatinizing temperature,[8] viscosity adhesion and resistance,[9] and power of gelatinization.[10]

Manufacture of Starch. The amount of starch obtainable

---

[1] C. Tanret, Compt. rend. 1909, **148**, 1775; abst. C. A. 1909, **3**, 2676; J. C. S. 1909, **96**, i, 556; J. S. C. I. 1909, **28**, 847; Bull. Soc. Chim. 1909, **5**, 310, 823; Rep. Chim. 1910, **10**, 66; Chem. Ztg. 1909, **33**, 837; Jahr. Chem. 1909, **62**, II, 374; Wag. Jahr. 1909, **55**, II, 226.

[2] Compt. rend. 1910, **150**, 710; **151**, 817; abst. J. C. S. 1910, **98**, i, 301, 817; J. S. C. I. 1910, **29**, 506; Chem. Zentr. 1910, **81**, I, 2074; Jahr. Chem. 1910, **63**, II, 408.

[3] M. Samec, Koll. Chem. Beihefte, 1912, **4**, 132; abst. J. S. C. I. 1913, **32**, 102; C. A. 1913, **7**, 3767; J. C. S. 1913, **104**, i, 17; Chem. Zentr. 1913, **84**, I, 632; Mayer Jahr. Chem. 1912, **22**, 430.

[4] F. Drittler, U. S. P. 847658, 847985, 1907. E. P. 7705, 1905; abst. J. S. C. I. 1906, **25**, 601.

[5] Zentr. Bakt. Par. 1908, II Abt. **22**, 98; 1911, II Abt. **29**, 188; abst. J. S. C. I. 1909, **28**, 153; 1911, **30**, 439; J. C. S. 1909, **96**, ii, 82; 1911, **100**, i, 181; Chem. Zentr. 1909, **80**, I, 68; 1911, **82**, II, 874.

[6] J. Thompson, E. P. 595, 1883.

[7] F. Norfolk, U. S. P. 480669, 1892. W. Marshall, U. S. P. 890524, 1908.

[8] C. Francis and O. Smith, J. Ind. Eng. Chem. 1916, **8**, 509; abst. J. S. C. I. 1916, **35**, 750; C. A. 1916, **10**, 2995.

[9] A. Binz, Flora, 1892, 34. Dissertation in München. A. Binz and T. Marx, Chem. Ind. 1909, **32**, 167; abst. J. S. C. I. 1909, **28**, 422; C. A. 1910, **4**, 2219; Chem. Zentr. 1909, **80**, I, 1509; Jahr. Chem. 1909, **62**, II, 375.

[10] A. Dox and G. Roark, J. A. C. S. 1917, **39**, 742; abst. J. S. C. I. 1917, **36**, 560; C. A. 1917, **11**, 1763. A. Meyer, Koll. Chem. Beihefte, 1913, **5**, 1; abst. J. C. S. 1913, **104**, ii, 848; C. A. 1914, **8**, 1225.

from a given area of ground depends upon the nature of the starch-producing plant cultivated; the percentage of starch contained therein; and the yield per acre. Whereas wheat contains some 55% of starch, and potatoes but 20%, yet twice as much potato starch can be obtained per acre as wheat starch, due to the fact that the yield per acre is 65 as to 13. Different varieties of the same species vary greatly in starch content. Ordinarily potato contains but 13% of starch, but in Germany by the careful selection and propagation of species, aided by suitable fertilization, the percentage of starch has been raised from 13% to 20% and even higher. The yield of starch is also governed by the age of the raw material, conditions of harvesting and exposure of raw material to extremes of heat and cold.

Over-ripe potatoes have been found to contain less starch, the loss being 3.2%–10%.[1] Barley exposed to moist weather so as to sprout, has been found to have lost 10% in starch content. Generally diseased potatoes contain less starch than normal ones, which is explained by the fact that the fungus attack converts some starch into sugar. Potatoes grown with highly nitrogenous manures are found to be more readily susceptible to attack by fungus. Freezing potatoes diminishes their starch content, the accepted explanation being that freezing converts a portion of the starch into sugar. The yield of starch is, of course, governed by the mechanical processes to which the raw material is subjected, as washing, defective machinery, or insufficient settling.

Wheat, potatoes, corn and rice are the usual raw materials from which starch is extracted, although cassava,[2] manioc,[3] tobacco leaves,[4] horse chestnut,[5] arrowroot,[6] mulberry,[7] locust

---

[1] E. Kramer, Bied. Centr. 1881, 717; abst. J. C. S. 1882, **42**, 242.

[2] Board of Trade Jour. May 26, 1904; abst. J. S. C. I. 1904, **23**, 636. Fiji. Bull. Imp. Inst. 1909, **7**, 271; abst. J. S. C. I. 1909, **28**, 1265. F. Perkins, U. S. P. 1020655, 1020656, 1912; abst. J. S. C. I. 1912, **31**, 453. E. Riboud and C. Ahnert, F. P. 462451, 1913; abst. J. S. C. I. 1914, **33**, 327.

[3] H. Milligan and A. Board, E. P. 5269, 1911; abst. J. S. C. I. 1912, **31**, 331. F. Strumberg, F. P. 472772, 1914; abst. J. S. C. I. 1915, **35**, 504. F. Norfolk, U. S. P. 480669, 1892. J. Dubiel, U. S. P. 493689, 1893. A. Lenders, E. P. appl. 5512, 1919. U. S. P. 1305291; abst. C. A. 1919, **13**, 2143.

[4] H. Müller-Thurgau, Landw. Jahr. 1880, **8**, 168; 1882, **11**, 751, 828; 1885, **14**, 485, 851, 909; abst. J. S. C. I. 1886, **5**, 169.

[5] C. Cross and E. Bevan, Ber. 1909, **42**, 2198; abst. J. S. C. I. 1909, **28**, 806. C. Cross and J. Remington, E. P. 1035, 1899; abst. J. S. C. I. 1899, **18**, 1038. Aust. P. 2186, 1900. L. Weil, E. P. 3217, 1901; abst. Chem. Ztg. 1902, **26**, 587.

[6] J. Macdonald, J. S. C. I. 1887, **6**, 334; abst. Jahr. Chem. 1887, **40**, 2662.

[7] H. Brunet, E. P. 2083, 1880.

beans,[1] beets,[2] cocao,[3] bread fruit,[4] apples,[5] bananas,[6] and others,[7] have been some of the sources from which it has been proposed to extract starch commercially. The starch from arrowroot, cassava and manioc are articles of commerce. Wheat which was formerly extensively used, has now been almost entirely replaced by potatoes, corn and rice. Corn is used almost exclusively in the United States, potatoes in Europe and rice in England.

Starch as an industry is concerned with production for three distinct purposes, i. e., (a) for laundry purposes; (b) for edible purposes, as in the manufacture of corn, arrowroot and tapioca starches; (c) as a size, dressing, or stiffening or filling material for paper, thickening of mordants in calico-printing, and the preparation of glucoses and syrups.

The history of starch is very ancient, although but little definite was known as to its composition until the commencement of the eighteenth century. The earlier processes of manufacture of starch in the United States[8] and in England,[9] are now mainly of historical interest, although many of the mechanical devices

---

1. A. Pinel, E. P. 13508, 1914; abst. J. S. C. I. 1915, **34**, 43.
2. J. Peklo, Bied. Zentr. 1911, **40**, 386; abst. J. C. S. 1911, **100**, ii, 763; C. A. 1912, **6**, 3205.
3. P. Trojanowsky, Arch. Pharm. (3), **10**, 32; abst. J. C. S. 1877, **32**, 363; Jahr. Chem. 1877, **30**, 937; Dingl. Poly. 1877, **223**, 650.
4. Bull. Imp. Inst. (Suppl. to Board of Trade J. 1904, **2**, 28); abst. J. S. C. I. 1904, **23**, 553.
5. G. Warcollier, Compt. rend. 1905, **141**, 405; abst. J. C. S. 1905, **88**, ii, 753; J. S. C. I. 1905, **24**, 981; Chem. Centr. 1905, **76**, II, 1266.
6. H. Waterman, Chem. Weekblad, 1915, **12**, 552; abst. J. C. S. 1915, **108**, i, 630; C. A. 1915, **9**, 2775.
7. W. Burton, E. P. 1160, 1866. W. Buttenshaw, West Ind. Bull. 1904, **5**, 1; abst. J. S. C. I. 1904, **23**, 672.
8. U. S. Patents, 563, 2000, 7850, 13340, 17710, 22460, 26084, 27130, 28278, 40693, 44405, 56356, 63754, 65664, 66121, 67514, 67515, 67516, 68294, 73259, 81888, 87607, 89510, 116597, 135904, 137911, 137912, 140141, 141442, 145213, 151085, 158104, 169054, 174587, 181751, 202832, 214910, 225149, 227583, 230344, 231528, 233124, 234119, 234680, 235053, 241554, 245340, 245663, 248973, 250335, 253923, 254029, 254063, 257108, 259732, 263958, 270210, 270894, 272324, 276806, 278490, 280044, 284983, 285901, 294530, 294531, 307366, 319315, 329701, 332439, 337490, 354409, 363235, 374346, 406559, 491234, 596265.
9. English Patents, 565, 872, 971, 997, 1377, 2370, 1855; 482, 496, 1661, 1748, 2533, 1856; 238, 617, 1226, 1235, 2801, 3001, 1857; 335, 452, 1076, 1325, 1932, 1858; 1640, 1980, 2006, 2077, 2256, 2564, 1859; 148, 611, 1050, 1181, 1454, 3038, 1860; 358, 940, 2162, 2456, 2903, 3138, 1861; 42, 1717, 3284, 3314, 1862; 2839, 1863; 782, 1624, 1957, 1864; 88, 1319, 1865; 2924, 1866; 82, 83, 2941, 3171, 1868; 933, 1897, 1869; 2102, 3956, 1872; 2007, 2307, 1875; 2370, 2694, 3236, 3517, 1876; 1492, 1968, 3226, 4501, 1877; 823, 1879; 340, 884, 937, 2631, 1880; 3314, 1881; 236, 1591, 2014, 4224, 4277, 1882; 4146, 1883; 3101, 1885; 3304, 5270, 6285, 1887; 24511, 1894.

evolved, have come down to the present time with but comparatively unimportant modifications.

The manufacture of starch from wheat and corn, may be subdivided into the older fermentation or "sour" process, and the Martin or non-fermentative process, the latter giving the higher yield from a raw product of the same starch percentage.

In the older method, the kernel was used either whole or ground, more often in the former condition, being steeped in water for some days, where a process of "retting" or decomposition takes place whereby the grain becomes much swollen and soft, the water being periodically renewed to wash away the soluble portions dissolved out. The swollen grain is then placed in bags and submitted to pressure until ruptured, the water which is expressed, being milky from starch, is run off into settling tanks for the starch to subside. The apparati of F. Kimball,[1] F. Matthiessen,[2] H. Humphrey,[3] A. Atkinson,[4] J. Schuman,[5] E. Roat,[6] J. Tonkin[7] and A. Murdoch[8] were used for this purpose. This alternate pressing and adding fresh water was repeated until nothing more was extracted (the expressed water was not milky), when the filtrates were combined in order to make a more homogeneous product, and run into cisterns where it was allowed to repose for from 10 to 30 days, depending upon the season of the year. During this period of subsidence fermentation sets in, which is accelerated by the addition of some of the sour liquid from a previous batch. Fermentation gradually frees the starch grain from its enveloping glutinous capsule, the latter becomes softened and passes more or less into solution, and completely loses its sticky and elastic properties. J. Jeffries separates by means of rotating reels,[9] C. Meyer[10] aids disintegration of the gluten

[1] U. S. P. 275340, 1883.

[2] U. S. P. 273572, 1883. F. Matthiessen and A. Behr, U. S. P. 257959, 1882. F. Mattiessen and E. Quimby, U. S. P. 257958, 1882.

[3] U. S. P. 231804, 1880. U. S. P. 250362, 1881.

[4] U. S. P. 253337, 1882; abst. J. S. C. I. 1882, **1**, 115.

[5] U. S. P. 316404, 316405, 316406, 318307, 318308, 320400, 320401, 320402, 334090, 341282, 341283, 344410, 344411, 344412, 345926, 346320, 345927, 379034.

[6] U. S. P. 254157, 254158, 254239, 254240, 1882.

[7] U. S. P. 258265, 1882.

[8] U. S. P. 717699, 717700, 1903; abst. J. S. C. I. 1903, **22**, 153. A. Murdoch and Improved Process Manufacturing Co., E. P. 319, 1903.

[9] J. Jeffries, U. S. P. 1007782, 1007783, 1007784, 1007785, 1911; abst. J. S. C. I. 1911, **30**, 1401. U. S. P. 1134615, 1915.

[10] E. P. 1146, 1894; abst. J. S. C. I. 1895, **4**, 55; Chem. Centr. 1895, **66**, I, 941.

by adding to the wash water a small percentage of chlorine, K. Peche[1] introduces specific bacteria, while H. Frasch[2] manipulates the process at a temperature below freezing, making the final separation by means of a perforated cylindrical corrugated iron drum.[3]

In the earlier stages of fermentation the natural occurring sugars of the grain, as well as any dextrin resulting from the action of the diastase upon unbroken starch grains, are converted into alcohol, and this oxidized into acetic acid. This fermentative process is continued until sufficiently far advanced to admit of the starch granules being separated in a state of comparative purity. The fermentation should, as far as possible, be confined to the acetic, lactic and butyric ferments, and actual putrefaction avoided as much as possible, due to the possibility of the starch granule being attacked and passing into water-soluble products. It is advizable to periodically agitate the mass during the fermentation process in order to equalize the action as far as possible.

As soon as the fermentation or ripening has progressed to the desired stage, the supernatant liquid is withdrawn and discarded, fresh water admitted, the contents well stirred and then allowed to settle until the liquid is clear, when it is again withdrawn. This is repeated until no more coloring matter is removed. After the final decantation, the starch will be found to have subsided in layers of different size particles of varying purity, the bottom layer being the purer. These layers are now roughly removed with a shovel and transferred to different vats, where they are agitated with water and passed through sieves of varying mesh. The processes of S. Gaunt,[4] E. Wilhelm,[5] C. Tremain,[6] V. Taschl,[7] W. Rochteschel,[8] T. Mueller,[9] L. Morel[10],

---

[1] D. R. P. 292864, 1914; abst. J. S. C. I. 1916, **35**, 937; Chem. Ztg. Rep. 1916, **40**, 275; Zts. ang. Chem. 1916, **29**, 359.

[2] U. S. P. 717184, 1902; abst. J. S. C. I. 1903, **22**, 153; Mon. Sci. 1903, **59**, 110; Chem. Zts. 1903, **2**, 375.

[3] G. Baugue, F. P. 424131, 1910; abst. J. S. C. I. 1911, **30**, 287; Mon. Sci. 1912, **77**, 116.

[4] U. S. P. 638707, 1899; 664257, 664258, 664259, 664260, 1900.

[5] U. S. P. 243024, 1881.

[6] U. S. P. 300165, 1888.

[7] U. S. P. 1057685, 1913. E. P. 15258, 1912; abst. J. S. C. I. 1913, **32**, 125. F. P. 446008, 1912; abst. J. S. C. I. 1913, **32**, 125.

[8] U. S. P. 538794, 1895.

[9] T. Mueller and J. Decastro, U. S. P. 273128, 1883.

[10] Addn. 285, dated March 25, 1902, to F. P. 300237, 1900; abst. J. S. C. I. 1903, **22**, 106.

A. Graves,[1] W. Allen[2] and W. Booth[3] give details of this portion of the process.[4]

The utilization or disposal of this refuse water is an important item in connection with the manufacture ofs tarch, especially as to its liability to pollution when passed into streams and interfering with the potability of the water.[5] G. de Claubry[6] precipitates with milk of lime and a tannin solution, and uses the sludge for manure; Markl[7] precipitates with lime. Other proposals are[8] to neutralize with soda and evaporate, or precipitate with alum; to extract the alcohol from the product after neutralization;[9] Burggraf[10] distributes it over meadow land in the raw state as a fertilizer, and Maercher[11] records definite results in support of the idea. R. Schuetze,[12] H. Schreib,[13] H. Seelos,[14] B. Steckel[15] and others[16] have also put forth suggestions.

After the starch has settled in the purifying vats, the supernatant water is decanted, and this process repeated until the wash water shows practically no total solids, indicating all the water soluble material has been removed from the starch substance. In this process N. and J. Bloch[17] uses a hollander with fine mesh screen, and T. Blumenthal[18] has described a continuous system of washing, which is said to greatly reduce the time of purification. The starch is then either removed from the vats by means of wooden shovels as in the manual method of C.

---

1. U. S. P. 246671, 248734, 250143, 251574, 1881; 256315, 1882; 270304, 1883; 362502, 1887.
2. U. S. P. 257318, 257319, 257320, 1883.
3. E. P. 3188, 1857. W. Booth and A. Bell, U. S. P. 256630, 1882.
4. I. Palmer, U. S. P. 222527, 1879; 304851, 1884; 346602, 1886.
5. Anon. Dingl. Poly. 1877, **225**, 394; abst. J. C. S. 1877, **32**, 943.
6. Dingl. Poly. 1837, **63**, 465; 1841, **80**, 399.
7. Dingl. Poly. 1874, **214**, 225.
8. See Dingl. Poly. 1838, **68**, 406.
9. J. Naylor, U. S. P. dated March 7, 1803.
10. Dingl. Poly. 1835, **56**, 464.
11. Zts. Landw. Central. Prov. Sachsen, 1876, 7.
12. Landw. Vers. St. **33**, 197; abst. J. S. C. I. 1886, **5**, 612.
13. Zts. ang. Chem. 1888, **1**, 694; abst. J. S. C. I. 1889, **8**, 127. Chem. Ztg. 1890, **14**, 1323; 1891, **15**, 1864.
14. Zts. f. Hyg. 1899, **31**, 469; abst. Zts. Untersuch. Nahr. u. Genussm. 1900, **7**, 503; J. S. C. I. 1900, **19**, 916; Chem. Centr. 1899, **70**, II, 158.
15. D. R. P. 74359, abst. Woch. f. Br. 1896, 276.
16. C. Peifke, Zts. Spiritusind. 1884, 219; Chem. Tech. Rep. 1884, **23**, I, 277. D. R. P. 25740 (second addn. to 15741). Chem. Ind. 1884, **7**, 237. Zts. Spiritusind. 1888, 373; 1894, 324. Mitth. ges. Stärke, 1890, 92; 1891, 140.
17. D. R. P. 4262, 1878.
18. D. R. P. 10579, 1880; abst. Wag. Jahr. 1880, **26**, 536.

Black[1] or the mechanical process of D. Wilder,[2] or else stirred up with water to a thin magma and allowed to flow over starch planes[3] where the starch deposits by gravity into a compact mass.[4] H. Holden removes the impurities from the liquor by entanglement in a voluminous froth produced by the injection of air, the froth being carried over into a separate receptable.[5] In the Verley method[6] nitrogenous and other impurities are eliminated by suspending the starch in water to form a milk of about 12° Bé., then agitating with a small portion of alkaline hypochlorite and allowing to stand for several hours.[7,8,9,10,11,12,13,14,15,16,17,18] S. Aston[19] advocates the use of fine cylindrical sieves for the final starch separation, while other mechanical devices have been patented for this purpose by R. Sherman,[20] G. Luthy[21] and more recently by W. Bartholomew and C. Leary.[22]

Irrespective of the method of transference of the starch, it

---

1. U. S. P. 1131318, 1915.
2. U. S. P. 1102376, 1914.
3. Davenport Glucose Manufacturing Co., E. P. 6166, 1885; abst. J. S. C. I. 1885, **4**, 542.
4. O. Steppacher, U. S. P. 1094175, 1914.
5. H. Holden, U. S. P. 1221990, 1917; abst. J. S. C. I. 1917, **36**, 607.
6. F. P. 330914, 1902; abst. J. S. C. I. 1903, **22**, 1097; Mon. Sci. 1904, **61**, 135; 1906, **65**, 39; 1909, **71**, 27.
7. G. Kandler, Aust. P. 32974, 1908.
8. P. Grimm, U. S. P. 258265, 261445, 264688, 296000, 303930, 354634, 440262.
9. E. Kesztler, Zts. Spiritusind. 1902, **25**, 249; abst. J. S. C. I. 1902, **21**, 982. Aust. P. 4538, 1901.
10. H. Lafferty, E. P. 9431, 1886; abst. J. S. C. I. 1886, **5**, 542.
11. M. Maercker, Landw. Versuch-Stat. **22**, 69; abst. J. C. S. 1878, **34**, 969. Landw. Stat. 1879, **23**, 69. Bied. Centr. 1880, 501; abst. J. C. S. 1880, **38**, 915. Zts. Spiritusind. 1883, 371, 391, 409, 501, 503; 1886, 204; 1887, 50. Zts. anal. Chem. 1885, **24**, 617. Maercker, Handbuch der Spiritusfabrikation, VI Aufl. 1894. M. Maercker, P. Behrend and A. Morgan, Vers.-Stat. 1880, **25**, 107.
12. W. Wiesebrock, E. P. 2208, 1885; abst. J. S. C. I. 1885, **4**, 358.
13. F. Moll, D. R. P. 35482, 1885. J. Moll, Bot. Instit. Würzburg, 1878, **1**, II, 105.
14. A. Parks, E. P. 8893, 1891; abst. J. S. C. I. 1891, **10**, 844.
15. E. Root, U. S. P. 254239, 254240, 1882; abst. J. S. C. I. 1882, **1**, 157. U. S. P. 254157, 254158, 1882; abst. J. S. C. I. 1882, **1**, 157.
16. F. Stiker, U. S. P. 270260, 320430, 327035, 327345.
17. F. and E. Verbiese, F. P. 361534, 1905. F. P. addn. dated June 5, 1905 to F. P. 361534, 1905; abst. J. S. C. I. 1906, **25**, 947.
18. T. Wagner, U. S. P. 816624, 1906. E. P. 2242, 1906; abst. J. S. C. I. 1906, **25**, 1229.
19. F. P. 452395, 1912; abst. J. S. C. I. 1913, **32**, 707.
20. U. S. P. 1147899, 1915.
21. U. S. P. 346820, 1886.
22. U. S. P. 1211385, 1917.

is next placed in canvas lined wooden boxes, 48 by 12 by 6 inches deep, where it is drained or dried into a compact mass. In the processes of J. Berrigan,[1] R. Wilson,[2] J. Foulis,[3] Gautron,[4] G. Hennig,[5] W. Jaeger-Koenkendorf,[6] G. Kerr,[7] F. Melkersman,[8] N. Miller,[9] M. Moll,[10] C. Rudolph,[11] R. Schrader,[12] de la Touche[13] and others,[14] the final separation is made by means of a centrifuge, which not only removes more water, but causes the starch to more firmly compact—which usually is desirable. When the maximum of moisture has been removed, the starch is taken from the box or centrifuge, and is cut into cubes of 4 to 5 inches on a side. In one method the cubes are placed upon porous bricks to absorb more water, and in such a manner that the under surface of the starch does not become hard and horny. Of the many methods which have been devized for this preliminary drying process, those of H. Neuberger and F. Bergh,[15] Harburger Stärke-Fabrik,[16] J. Lyman,[17] W. Liess and M. Maher,[18] W. Lenders,[19] C. Haug and H. Magnuson,[20] E. Gudeman,[21] C. Drumm,[22] Drumm & Co.,[23] O. Beusterien[24] and A. Baroody[25] appear to be the

1. U. S. P. 994497, 1911; abst. J. S. C. I. 1911, **30**, 914.
2. E. P. 10956, 1894; abst. J. S. C. I. 1895, **14**, 590.
3. D. R. P. 35260, 1885.
4. Dingl. Poly. 1863, **169**, 315.
5. Zts. Spiritusind. 1883, 526; 1884, 4.
6. D. R. P. 43550, 1888; abst. Zts. Spiritusind. 1888, 283; Wag. Jahr. 1888, **34**, 590.
7. U. S. P. 471614, 473511.
8. U. S. P. 195718, 1877.
9. U. S. P. 235001, 1880.
10. D. R. P. 33677, 1885.
11. D. R. P. 18712, 1881; abst. J. S. C. I. 1882, **1**, 415; Wag. Jahr. 1882, **28**, 684; 1883, **29**, 670. D. R. P. 19593, 1882; addn. to D. R. P. 18712, 1881; abst. J. S. C. I. 1882, **1**, 464.
12. U. S. P. 757778, 1904; abst. J. S. C. I. 1904, **23**, 554.
13. Dingl. Poly. 1850, **118**, 236; Mon. Ind. 1850, 1494.
14. Anon. le Technologiste, 1859, 32; abst. Poly. Centr. 1859, **25**, 1697; Dingl. Poly. 1860, **155**, 237.
15. U. S. P. 1047831, 1912; abst. J. S. C. I. 1913, **32**, 102; C. A. 1913, **7**, 914; Chem. Ztg. Rep. 1913, **37**, 250.
16. F. P. 376767, 1907; abst. J. S. C. I. 1907, **26**, 980. Aust. P. 45188, 1910. F. Thörl, U. S. P. 990929, 1911. E. P. 9931, 1907; abst. J. S. C. I. 1907, **26**, 980. D. R. P. 206763.
17. U. S. P. 721314, 1903; Mon. Sci. 1903, **59**, 101.
18. U. S. P. 284447, 1883. W. Lies, U. S. P. 275394, 1883.
19. U. S. P. 1223406 1917; abst. J. S. C. I. 1917, **36**, 607.
20. U. S. P. 1162771, 1915.
21. U. S. P. 789127, 1905.
22. D. R. P. 217335, 1908; abst. J. S. C. I. 1910, **29**, 710; Wag. Jahr. 1910, **56**, II, 258; Chem. Zentr. 1910, **81**, I, 492; Chem. Ztg. Rep. 1910, **34**, 46.
23. E. P. 5260, 1884.
24. E. P. 12624, 1895.
25. U. S. P. 844911, 1907.

most meritorious.[1] H. and R. Littmann[2] compress the starch into spheres. A novel method of compacting has been put forward,[3] which consists in dropping the starch through a zone of steam and hot air which superficially gelatinizes the starch and causes it to adhere into lumps.[4]

At the conclusion of this preliminary drying, the starch contains from 25% to 30% of water. The remaining moisture may be removed by placing the starch in wagons having foraminous sides,[5] or in trays with cloth bottoms,[6] and subjecting to a heat of 45°–55°, until the desired moisture content is reached, the drying being carried on at atmospheric pressure, or, as in the processes of E. Passburg[7] and L. Maische,[8] under partial vacuum. C. Vidal[9] and C. Pope[10] dry under hydraulic pressure, the latter at 500 pounds per square inch.[11–24] The Banque du Radium[25] bleach and preserve the finished starch by placing the flour on a traveling band which passes beneath a quartz plate fitted in a chamber

---

1. M. Petersen, E. P. 11416, 1899; abst. J. S. C. I. 1899, **18**, 776. U. S. P. 649210, 1900.
2. E. P. 1651, 1905. See also E. P. 1661, 1879; 12624, 1895.
3. H. Neuberger and F. Bergh, U. S. P. 1047831, 1912.
4. W. Lake, E. P. 4957, 1885.
5. L. Bauer, U. S. P. 1035302, 1912; abst. J. S. C. I. 1912, **31**, 1089. E. P. 13984, 1912.
6. N. Yagn, E. P. 5225, 1905; abst. J. S. C. I. 1906, **25**, 86.
7. D. R. P. 28971, 1884.
8. D. R. P. 23355, 1882; abst. J. S. C. I. 1884, **3**, 113.
9. E. P. 1661, 1879. D. R. P. 6969, 1879.
10. U. S. P. 595408, 1897.
11. H. Benoist, F. P. 425430, 1911; abst. J. S. C. I. 1911, **30**, 914. H. Benoist and L. Graillot, F. P. 373174, 1907; abst. J. S. C. I. 1907, **26**, 704.
12. F. Wiesebrock, D. R. P. 34950, 1885. U. S. P. 312592, 312593, 333908, 346003. E. P. 2208, 1885.
13. Wever, Zts. Spiritusind. 1892, 9. Landw. Centr. f. Prov. Posen, 1892, 311.
14. C. Schöngart, D. R. P. 13678, 1880.
15. E. Perkins, U. S. P. dated Sept. 16, 1810. U. S. P. 815373, 1906; abst. J. S. C. I. 1906, **25**, 385.
16. J. Merrill, U. S. P. 1183097, 1916; abst. J. S. C. I. 1916, **35**, 858.
17. R. Johnson, U. S. P. 227537, 1880; 323425, 1885.
18. J. Hundhausen, U. S. P. 603447, 1898. E. P. 22918, 1895; abst. J. S. C. I. 1896, **15**, 887. D. R. P. 80922, 1894. Zts. Spiritusind. 1895, 225.
19. J. Görlt, D. R. P. 23590, 1882.
20. G. Full, U. S. P. 260188, 1882.
21. C. Fehrmann, D. R. P. 29600, 1884. Dingl. Poly. 1885, **256**, 35; abst. J. S. C. I. 1885, **4**, 356.
22. L. Bauer, U. S. P. 583783, 1897; 1035302, 1912; abst. J. S. C. I. 1912, **31**, 1089. 1061720, 1912; abst. J. S. C. I. 1913, **32**, 669. 1099276, 1914. 1101071, 1914; abst. J. S. C. I. 1914, **33**, 801. 1161826, 1915; abst. J. S. C. I. 1916, **35**, 134. 1175113, 1175114, 1916; abst. J. S. C. I. 1916, **35**, 482. L.

containing an arc lamp, a Geissler tube, a mercury vapor lamp, or other source of ultraviolet or similar rays.[1-13] J. Harley[14] dries starch in an atmosphere charged with steam, the claim being that the starch is rendered less brittle.[15] If the starch is to be powdered ("depulverized") before being offered for sale, the methods of P. Dreesbach,[16] J. Benoid[17] or W. Bust[18] may be used. Starch for nitration or acetation must be free from oil. This may be removed by chloroform,[19] ligroin or carbon tetrachloride extraction.[20]

In Martin's process, flour instead of the whole grain is employed, the first operation being kneading into a stiff dough as in bread-making, when it is allowed to remain at rest until the mass becomes thoroughly and uniformly saturated with moisture.

Bauer and T. Speck, U. S. P. 986540, 986541, 1911; abst. J. S. C. I. 1911, **30**, 503.

[23] Corn Products Refining Co., F. P. 445289, 1912; abst. J. S. C. I. 1912, **31**, 1089.

[24] Sudenburger Maschinenfabr. and Eisengiesserei A. G., D. R. P. 261259, 1912; abst. J. S. C. I. 1913, **32**, 837.

[25] F. P. 428969, 1910; abst. J. S. C. I. 1911, **30**, 1276.

[1] M. Blumenwitz, Uhland Mach. Construc. 1874, No. 11, 173. Böhmer, D. R. P. 22332, 1882. A. Büttner and C. Meyer, D. R. P. 34031, 1884. D. R. P. 45080, 1888; 52578, 1889; 61659, 1891; 68074, 1892; 69808, 1892. W. Gintl, Dingl. Poly. 1874, **214**, 221. J. Habrich, D. R. P. 29985, 1884. F. Köchlin, Dingl. Poly. 1851, **120**, 364. G. Lindenmeyer, Dingl. Poly. 1868, **189**, 131. E. Nussbaum, E. P. 15700, 1907. H. Rodewald, Vers.-Stat. 1894, **45**, 201. R. Schmidt, Dingl. Poly. 1863, **169**, 257; 1865, **177**, 116. Schönn, Dingl. Poly. 1870, **195**, 469. A. Winton, Zts. ang. Chem. 1888, **1**, 273. Zts. Spiritusind. 1888, 188; 1889, 326, 361; 1890, 289, 368; 1894, 51, 391.

[2] J. Hurty, U. S. P. 395977, 1889.

[3] H. Wiegand, U. S. P. 392389, 1888.

[4] J. Van Deinse and M. Reiseger, U. S. P. 444127, 1891.

[5] J. Rubiel, U. S. P. 493689, 1893.

[6] J. Ostenburg, U. S. P. 447790, 450492, 1891.

[7] A. Moffatt, U. S. P. 541941, 545128, 1895.

[8] J. O'Neill, U. S. P. 584399, 1897.

[9] U. S. P. 509512, 1893.

[10] J. and F. Firmenich, U. S. P. 260380, 1882. J. and G. Firmenich, U. S. P. 560699, 1896.

[11] C. Gordon, U. S. P. 596058, 1897.

[12] A. Osborn, U. S. P. 746369, 1903.

[13] C. Tyler, U. S. P. 1013337, 1912; 1157738, 1915; abst. J. S. C. I. 1915, **34**, 1220. 1190690, 1916.

[14] U. S. P. Re- 1123, 1883.

[15] M. Holaubek, F. P. 353730, 1905; abst. J. S. C. I. 1905, **34**, 1079.

[16] U. S. P. 1186893, 1186894, 1916; abst. J. S. C. I. 1916, **35**, 860.

[17] U. S. P. 867235, 1907. E. P. 14205-A, 1906.

[18] U. S. P. 1046261, 1912.

[19] G. Hertel and G. Hornung, D. R. P. 220850, 220851, 1909; abst. J. S. C. I. 1910, **29**, 649.

[20] E. Carez and Soc. Gen. du Maltose, E. P. 3606, 1890.

This requires from 30 to 60 minutes, depending upon the surrounding temperature. For the separation of the starch from the gluten the dough is placed in a wooden trough containing a rectangular frame which mechanically oscillates. Above the trough fine jets of water impinge upon the dough which is mechanically kneaded, the wash water running away into settling cisterns, where the starch is allowed to subside. The dough before washing is subdivided into small balls for convenience in extracting the starch, washing being continued until substantially only the gluten remains, and until the wash water runs nearly clear. Should any particles of gluten become detached and mingle with the wash water, they are caught by a trap arrangement.

The purification of the starch is effected in much the same manner as previously described by means of repeated decantations. Martin improved upon his original process, by supplanting washing with pure water, by washing with dilute sodium hydroxide solution. While this does give a better product, much experience and care is required to keep the proper alkalinity at the various stages of the washing process. In starch produced in this manner, excellent results are obtained by drying in the R. Wilson apparatus.[1-7]

In W. Uhland's apparatus the grain is first fed through a hopper to a pair of crushing rollers together with dilute alkali,[8] where it falls into a mixing chamber provided with a pair of revolving beaters.[9] The pure starch obtained is separated from the crude by mechanical means.[10] In the block process of drying, he[11] mechanically removes the yellowish layer which forms upon starch blocks during the drying process.[12]

1. E. P. 10956, 1894.
2. G. Pereire, F. P. 333110, 1903; abst. J. S. C. I. 1903, **22**, 1301.
3. J. Grossfeld, Zts. Unters. Nahr. Genussm. 1915, **29**, 51; abst. Zts. ang. Chem. 1915, **28**, 223 R; J. S. C. I. 1915, **34**, 676.
4. O. Froberg, U. S. P. 1158040, 1915.
5. C. Moore, U. S. P. 1016761, 1912.
6. J. Hilton, E. P. 25242, 1894; abst. J. S. C. I. 1895, **14**, 376.
7. C. Tyler, U. S. P. 1013337, 1912.
8. E. P. 4256, 1883.
9. E. P. 425, 1905; abst. J. S. C. I. 1905, **24**, 629.
10. E. P. 14428, 1900; abst. J. S. C. I. 1901, **20**, 916.
11. E. P. 23866, 1897.
12. U. S. P. 725180, 1903; abst. J. S. C. I. 1903, **22**, 642. 784450, 1905; abst. J. S. C. I. 1904, **23**, 795. 860068, 1907. F. P. 338792, 1903; abst. J. S. C. I. 1904, **23**, 795. 348992, 1904; abst. J. S. C. I. 1905, **24**, 629. D. R. P. 26521, 36250, 37231, 40922, 79245, 79961, 126203, 135312, 159088,

W. Jebb.[1-9] W. Klopfer,[10,11] A. Anderson,[12] A. Hoyt,[13-15] C. Moore,[16,17] F. Kaehl,[18] J. Loiselet,[19] A. Schumann,[20] H. Vivien,[21] A. Boerner,[22] S. Lillie,[23] and F. Klopfer[24] are, among others,[25] the

---

159351, 174624, 251907, 1911; abst. J. S. C. I. 1913, **32,** 41. 267199, 1911; abst. J. S. C. I. 1914, **33,** 36. Aust. P. 9150, 1902; 14885, 1904; 24086, 25506, 1906; 29068, 1907; 59129, 1913.

[1] J. Jebb, U. S. P. 270439, 1883.

[2] T. Jebb and A. Bennett, E. P. 3366, 1880.

[3] T. and W. Jebb, U. S. P. 239171, 241666, 243269, 243270, 249056, 256221, 258070.

[4] E. P. 386, 1881.

[5] W. Jebb, U. S. P. 263525, 320361, 347611, 347612.

[6] W. Jebb, E. P. 995, 1882; abst. J. S. C. I. 1882, **1,** 376. E. P. 4209, 1882.

[7] W. Jebb, E. P. 4948, 1885; abst. J. S. C. I. 1885, **4,** 748. E. P. 4954, 1885; abst. J. S. C. I. 1885, **4,** 748. E. P. 4956, 6139, 1885.

[8] W. Jebb, E. P. 508, 1886.

[9] W. Jebb, D. R. P. 17815, 1881; abst. J. S. C. I. 1882, **1,** 242.

[10] U. S. P. 929861, 1909; abst. J. S. C. I. 1909, **28,** 999. 1013497, 1912; abst. J. S. C. I. 1912, **31,** 144. E. P. 11159, 1907; abst. J. S. C. I. 1907, **26,** 1289. E. P. 19726, 1908; abst. J. S. C. I. 1909, **28,** 379.

[11] F. P. 394802, 1908; abst. J. S. C. I. 1909, **28,** 379. D. R. P. 200774. Aust. P. 38297, 1909.

[12] U. S. P. 707892, 1902; 1035829 to 1035842, 1912; abst. J. S. C. I. 1912, **31,** 944, 945. 1129440, 1915. E. P. 13353, 1902; abst. J. S. C. I. 1902, **21,** 1189. 18946, 18949, 18950, 1912; abst. J. S. C. I. 1912, **31,** 944, 945. F. P. 321842, 1902; abst. J. S. C. I. 1902, **21,** 1189.

[13] U. S. P. 709544, 1902; abst. J. S. C. I. 1902, **21,** 1288. 710461, 1902; 1148453, 1148454, 1915; abst. J. S. C. I. 1915, **34,** 917.

[14] E. P. 9790, 1915; abst. J. S. C. I. 1915, **34,** 702.

[15] F. P. 479236, 1915; abst. J. S. C. I. 1915, **34,** 1029. Aust. P. 75153, 1915.

[16] U. S. P. 1016761, 1016762, 1912; abst. J. S. C. I. 1912, **31,** 245; 1156801, 1915; abst. J. S. C. I. 1915, **34,** 1157. 1224951, 1917; abst. J. S. C. I. 1917, **36,** 607.

[17] E. P. 22655, 1909; abst. J. S. C. I. 1909, **28,** 1123. E. P. 530, 1914; abst. J. S. C. I. 1914, **33,** 1217.

[18] D. R. P. 155562, 1903; abst. J. S. C. I. 1905, **24,** 629.

[19] U. S. P. 702571, 1902; abst. J. S. C. I. 1902, **21,** 982.

[20] E. P. 5459, 5460, 1887; abst. J. S. C. I. 1888, **7,** 334, 335.

[21] E. P. 16827, 1886; abst. J. S. C. I. 1888, **7,** 41.

[22] E. P. 16262, 1904; abst. J. S. C. I. 1905, **24,** 808. F. P. 345370, 1904; abst. J. S. C. I. 1904, **23,** 1229.

[23] U. S. P. 1014311, 1023257, 1038397, 1912.

[24] U. S. P. 1013497, 1912.

[25] H. Barker, E. P. 4741, 1889; abst. J. S. C. I. 1889, **8,** 633. Improved Process Manufacturing Co., F. P. 328293, 1903; abst. J. S. C. I. 1903, **22,** 957. G. Goldbeck, Chem. Ztg. 1915, **39,** 680; 1916, **40,** 829; abst. J. S. C. I. 1915, **35,** 1065; 1916, **35,** 1169. J. Keil, E. P. 17444, 1897; abst. J. S. C. I. 1897, **16,** 927. H. Keil and R. Stoltenhoff, E. P. 6778, 1888; abst. J. S. C. I. 1889, **8,** 298. H. Longsdon and J. Mahon, E. P. 11089, 1907. W. Midgley, U. S. P. 319598, 1885; Re-10722, 1886. J. Polson and J. Harley, E. P. 2703, 1883; abst. J. S. C. I. 1884, **3,** 113. U. S. P. 285067, 1883. S. Spitzer, U. S. P. 329229, 1885; 361788, 1887; 386363, 1888. E. P. 4181, 1890; abst. J. S. C. I. 1890, **9,** 754. H. Sulman and E. Berry, E. P. 2138, 1887; abst. J. S. C. I. 1887, **6,** 375. C. Tolhurst and A. Goldthwaite, U. S. P. 707985, 707986, 1902; abst. J. S. C. I. 1902, **21,** 1190. H. Vuylsteke, E. P. 21344, 1894.

more important of those who have suggested improvements upon the basic process as outlined above. C. Dobrin[1] has called attention to the fact that the seeds of different sorghums contain about 60% of starch and has devised a process for its extraction.

Manufacture of Starch from Potatoes. In the earlier days of starch manufacture, considerable quantities were produced in the United States and Great Britain from potatoes, but in France and Germany—especially the latter country—more attention has been paid to the development of the potato from the view-point of starch producing, and, as has been previously stated, the Germans by cross-fertilization, selection of species and fertilization, have been able to raise the average starch content of these tubers from 25%–40%. In these two latter countries not only is the home market supplied, but large quantities are annually exported in normal times. The earlier processes developed in Germany[2] and in France,[3] are advancements primarily due to agricultural chemical research.

As the result of the examination of 61 varieties of potatoes, L. Raab[4] found the total solids to vary from 16%–34%, and the starch content from 9%–26%.[5] In a series of comparative tests on the cultivation of potatoes, in which thirty-seven varieties were examined, H. Nitykowski[6] found the yield to vary from 9697 k. per 5000 sq. m. to 4167 k. per 5000 sq. m.[7] Tables for the calculation of the relation between the quantity of starch in potatoes and their relative density have been prepared.[8] F.

---

[1] Zts. Spiritusind. 1897, **20**, 418; abst. J. S. C. I. 1898, **18**, 59.

[2] The following are German Patents on the manufacture of potato starch: 528, 2686. 10242, 10497, 10899, 11404, 13279, 15428, 16373, 17470, 19754, 20344, 21358, 21786, 21889, 22622, 22716, 24312, 24502, 24629, 25755, 26115, 26202, 28277, 28356, 28401, 29025, 33625, 35693, 36569, 45284, 52781, 56558.

[3] F. P. 62285, 62618, 62759, 68271, 68368, 69065, 70176, 70223, 70771, 75542, 77064, 77650, 78826, 79195, 79644, 80194, 81176, 81213, 82059, 85604, 86843, 87622, 88227, 90985, 106658, 114381, 114927, 116114.

[4] J. C. S. 1872, **25**, 1111; abst. Chem. Centr. 1872, **43**, 424; N. Jahr. Pharm. **37**, 204; Jahr. Chem. 1872, **25**, 804.

[5] A. Fesca, Dingl. Poly. 1868, **187**, 435; Wochenbl. preuss. Ann. Landw. 1867, No. 48; Poly. Notizbl. 1868, **23**, 97; Poly. Centr. 1868, **34**, 696; Wag. Jahr. 1868, **14**, 454.

[6] Dingl. Poly. 1883, **248**, 381; abst. J. C. S. 1884, **46**, 134; Jahr. Chem. 1883, **36**, 1745; Wag. Jahr. 1883, **29**, 668.

[7] O. Abesser, Zts. Landw. Centr. Provinz Sachsen, 1874, 204.

[8] F. Heidepriem. Landw. Vers. Stat. 1877, **20**, 1; abst. J. C. S. 1877, **32**, 233; Bull. Soc. Chim. 1878, **29**, 92; Chem. Tech. Rep. 1877, **16**, I, 363; Jahr. Chem. 1877, **30**, 1208.

Lankow[1] claims that potatoes may be preserved without first being subdivided, by freezing, thawing, pressing and drying, and that a material rich in sugar is produced by freezing slowly for a long time, and one high in dextrin and starch by freezing rapidly.[2]

The manufacture of potato starch on the Continent comprises the distinct operations of steeping, washing, disintegrating, removal of the starch, purification, washing, draining and drying, either centrifugally or in the air.[3]

Potatoes which have been raised on heavy ground are covered with adherent dirt so tenaciously that simple washing is not sufficiently energetic treatment to remove the dirt, and they are given a preliminary soaking in clear water for several hours,[4] and then washed in a hollow revolving cylinder, the periphery of which is composed of heavy wire of large mesh, in order to admit of the softened dirt running out.[5] This cylinder is partly immersed in a trough of water, revolving slowly, the friction of the potatoes rubbing against each other being sufficient to effectually remove all extraneous impurities. The operation is continuous, the potatoes being fed in at one end, and emerging cleaned at the other, where they fall into a rasping[6] or grating machine,[7] where the starch cells are ruptured, and a critical step

---

[1] E. P. 1048, 1905; abst. J. S. C. I. 1905, **24**, 1182.

[2] E. Schulze, Ber. 1874, **7**, 1047; abst. Chem. Centr. 1874, **45**, 645; Chem. Tech. Rep. 1874, **13**, II, 144; Dingl. Poly. 1874, **214**, 339. J. prakt. Chem. 1883, **136**, 311; abst. J. C. S. 1884, **46**, 284. Zts. Spiritusind. 1883, 1037; 1884, 109; 1887, 12; 1888, 341. Chem. Ztg. 1891, **15**, No. 29; Zts. Spiritusind. 1894, No. 18. E. Schulze and Barnieri, Vers.-Stat. 1878, **21**, 63. E. Schulze, J. Barbiere and Engster, Landw. Vers.-Stat. **21**, 63; **27**, 357. E. Schulze and E. Eugster, Vers.-Stat. 1882, **27**, 357; abst. Zts. Spiritusind. 1883, 25. E. Schulze and M. Maercker, J. Landw. 1872, 52. E. Schulze and Seliwanoff, Vers.-Stat. 1887, **34**, 403.

[3] B. Fricker, Zts. Spiritusind. 1885, 76, 120. D. R. P. 39144, 1886. Verein der Spiritus-Fabr. D. R. P. 286106, 291307, 291308; abst. J. S. C. I. 1916, **35**, 192; 1919, **38**, 595-A. v. Eckenbrecher, Zts. Spiritusind. 1888, 15; 1894, 33, 210; 1895, 27. H. Czubata, Bied. Centr. f. Landw. 1880, I, 472. See C. Putsche translation of A. Dubief, "Starchmeal from Potatoe," 1831. F. Anthon, Dingl. Poly. 1859, **154**, 69. Zts. Spiritusind. 1893, 375. Andrew, Dingl. Poly. 1843, **87**, 396.

[4] G. Gerson, Zts. Spiritusind. 1883, 723; 1884, 57; abst. Chem. Tech. Rep. 1885, **24**, I, 178; Chem. Ztg. 1885, **9**, 602; Jahr. Chem. 1883, **36**, 1726.

[5] Champannois, Dingl. Poly. 1867, **183**, 351; **186**, 193; J. Fabricantes de Sucre, 1867, Jan. 3d; Bull. Soc. d'Encouragement, 1867, 390.

[6] C. Steffen, E. P. 24035, 1906; abst. J. S. C. I. 1907, **26**, 883. F. P. 368002, 1906; abst. J. S. C. I. 1906, **25**, 1230. Addn. dated Dec. 12, 1906, to F. P. 368002, 1906; abst. J. S. C. I. 1907, **26**, 710. Aust. P. 37417, 1909; 41706, 1910.

[7] H. Tryller, D. R. P. 242168, 1910; abst. J. S. C. I. 1912, **31**, 505; Wag. Jahr. 1912, **58**, II, 339; Chem. Zentr. 1912, **83**, I, 388; Chem. Ztg. Rep. 1912, **36**, 61; Zts. ang. Chem. 1912, **25**, 924; C. A. 1912, **6**, 2190.

in the process is to be assured that the highest possible percentage of cells are ruptured, since it is from these only that the starch granule is removed.[1]

In order to separate the starch from the coarser bits of fiber, the pulp is washed with water over brass sieves of varying degrees of fineness, and the coarser portions retained on the sieve. Several forms of apparatus have been designed for this purpose,[2] the object being to completely exhaust the pulp in the shortest possible time with the minimum amount of wash water. A slight increase in starch is obtainable by grinding the pulp after rasping, factory practice indicating an increase of starch by 7%–10%.[3] As the starchy liquor comes from the sieves, it usually contains some fine sand which was not separated during the washing of the potatoes, and was too fine to be held back by the sieves. The starch liquor is therefore run into large tanks provided with agitators, where the solution is vigorously stirred, and allowed to remain at rest just long enough to allow the sand particles to deposit, when the liquor is run off into other containers and the impure starch allowed to subside.[4]

After several washings, sometimes in slightly alkaline water,

---

1. L. Günther, Zts. Spiritusind. 1884, 93. D. R. P. Dec. 24, 1880. Zts. Spiritusind. 1886, 126. D. R. P. Jan. 25, 1881. E. Wollny, Saat und Pflege der Landw. Kulturpflanzen, 1885, 141. Forschungen Gebiete der Agrikulturphysik, 1891, **14**, 286. Völkers, Dingl. Poly. 1840, **76**, 213. F. Stohmann, Wag. Jahr. 1859, **5**, 328. Zts. anal. Chem. 1870, **9**, 275. W. Snell, Dingl. Poly. 1844, **93**, 281. Schattenmann, Dingl. Poly. 1853, **130**, 72; Mon. Ind. 1853, No. 1789. J. Nessler, Dingl. Poly. 1871, **200**, 342. G. Neuhauss, Zts. Spiritusind. 1886, 464. O. Lorenz, Prakt. Machinconstr. 1883, 311, 323. Zts. Spiritusind. 1894, 77; 1896, 88. Dingl. Poly. 1846, **101**, 426. J. Hannay, Dingl. Poly. 1877, **223**, 548; Chem. News, 1876, **34**, 155. L. Foissey, Zts. Spiritusind, 1895, 159.

2. H. Werner, "Die Aufbewahrung der Kartoffel. Kartoffelbau, 1895, 3 Ed. 170. Dingl. Poly. 1845, **97**, 1158. Dingl. Poly. 1877, **225**, 394.

3. H. Eichhorn, Ann. Phys. Chem. 1852, **87**, 227. F. Cloez, Dingl. Poly. 1874, **211**, 397; abst. J. C. S. 1874, **27**, 1015; Bull. Soc. d'Enc. 1873, 553. A. Clerget, Dingl. Poly. 1846, **99**, 71. v. Canstein, Bied. Centr. 1878, I, 368. A. Baudry, La Feculerie (Compiegne), 1892, 11. D. R. P. 85889, 1895.

4. B. Dietzell, Dingl. Poly. 1869, **193**, 233. B. Frank, Zts. Spiritusind. 1896, 136. B. Frank and F. Krüger, Arbei. Deut. Landw. Ges. 1894, II. Zts. Spiritusind. 1896, 1. B. Frank and Sorauer, Deut. Landw. Ges. 1892. F. Heine, Zts. Spiritusind. 1883. E. Hahn, Zts. Spiritusind, 1894, 154. F. Holdefleiss, Landw. Jahr. 1877, **6**, I Suppl. 107. See Hornung and Scheibner, "Neues Einmietungsverfahren für Rüben und Kartoffeln mit selbstthätiger Ventilation," Berlin, 1891. Huck, Dingl. Poly. 1846, **102**, 361. J. Hungerbuhler, Vers. Stat. 1886, **32**, 387. H. Karsten, Vers. Stat. 1865, **7**, 490. E. Kramer, Bied. Centr. 1881, 717; abst. J. C. S. 1882, **42**, 242. Oest. Landw. Centr. 1891, 11. U. Kreusler, Landw. Jahr. 1886, **15**, 309. U. Kreusler and F. Dafert, Landw. J. 1894, 767. Krocker, Dingl. Poly. 1849, **112**, 143; Berz. Jahr. 1848, **27**, 391; Ann. 1846, **58**, 212.

the purified starch solution is passed through a fine wire sieve and allowed to settle until the supernatant liquid is entirely clear, which is then decanted, the surface of the starch scraped in order to remove a yellowish layer, and the mass finally divided into cubes and allowed to dry.[1] The economic disposal of the large amount of wash water in connection with the manufacture of potato starch has been critically studied by M. de Leeves,[2] J. Halmi,[3] G. Foth[4] and W. Kette-Jassen.[5]

In the process of R. Goldschmidt and J. Hasek,[6] the rasped potato is agitated in a centrifugal with dilute mineral acid until the liquors which run away are free from starch. The solid residue remaining is then reduced to a paste by the addition of a mineral acid if dextrin is required, or if not, is dried, ground, sifted and boiled, the starch being used as such or converted into amylaceous products.[7]

Recently H. Ducomet and A. Girard[8] have published the results of work on the utilization of rotten potatoes in the manufacture of starch, in which they find that spoiled potatoes are suitable, provided decomposition has not been carried very far. According to their observations, even when the tubers are in a

---

[1] J. Lemmon, Zts. Spiritusind. 1883, 139; Agricultural Gaz. 1883, Jan. 8. F. Lüdersdorff, Dingl. Poly. 1841, **79**, 313. G. Marek, Jahr. Deut. Landw. 1892, **7**, 208. C. Marx, Schweiggers J. 1829, **56**, 478. A. Morgen, Deut. Landw. 1879, 533. F. Nobbe, Vers. Stat. 1865, **7**, 451. W. Paulsen, Zts. Spiritusind. 1895, 405. E. Pott, Wiener Landw. Ztg. 1875, 168. E. Ring, Deut. Landw. Presse, 1891, No. 22, 205.

[2] Zts. Landw. Centr. Ver. Sachsen, 1876, No. 7, 171.

[3] Vizügyi Kozlemények, 1916, **6**, 1; Bull. Agric. Intell. 1916, **7**, 736; J. S. C. I. 1916, **35**, 1126; C. A. 1917, **11**, 2518.

[4] G. Foth, Zts. Spiritusind. 1911, **34**, 25; abst. J. S. C. I. 1911, **30**, 147; Wag. Jahr. 1911, **57**, II, 393; Zts. ang. Chem. 1911, **24**, 649, 1548.

[5] Zts. Spiritusind. 1883, 662. Bied. Centr. 1884, 122; abst. J. C. S. 1884, **24**, 948. Wochenschr. der P. rek. Ges. 1884, No. 4; abst. J. S. C. I. 1884, **3**, 575; Bied. Centr. 1884, **13**, 355; Chem. Ztg. 1884, **8**, 862; Chem. Tech. Rep. 1884, **23**, I, 183. D. R. P. 7518, 1879; 10033, 1879; 10836, 1879.

[6] U. S. P. 755479, 1904; abst. J. S. C. I. 1904, **23**, 449. F. P. 331061, 1903; abst. J. S. C. I. 1903, **22**, 1142. Aust. P. 19064, 35059.

[7] A. Girard, Compt. rend. 1887, **104**, 1629; abst. J. C. S. 1887, **52**, 868. Anon. Dingl. Poly. 1883, **248**, 381; abst. J. S. C. I. 1883, **2**, 419. Zts. Spiritusind. **19**, 385; abst. J. S. C. I. 1896, **15**, 913. Rahm, Zts. Spiritusind. 1891, 73. C. Sajo, Oest. Landw. Wochenbl. 1896, No. 24, 185. F. Schertler, "Die Anwendung des spec. Gewichts als Mittel zur Werthbestimmung der Kartoffeln, Cerealien und Hülsenfrüchte," Wien, A. Hartleben, 1873. W. Schultze, Dingl. Poly. 1871, **202**, 86. A. Semplowski, Zts. Pflanzenkrankheiten, 1895, **5**, 203.

[8] Compt. rend. l'Acad. Agric. France, 1917, **3**, 761; Bull. Agric. Intell. 1917, **8**, 1191; J. S. C. I. 1917, **36**, 1283; C. A. 1918, **12**, 1708.

deliquescent state, the starch is still undecomposed, and only at a later stage does the starch undergo liquefaction. It is therefore advizable to collect all potatoes attacked by damp rot, whether caused by frost, mildew or otherwise, and extract the starch, which, after proper purification, is fit for consumption by man or beast. The period during which spoiled potatoes can be kept for treatment may be considerably prolonged by covering them with water and renewing this from time to time.[1] The decomposition of starch during fermentation has been investigated by M. Delbrück.[2]

In order to remove the peculiar odor which sometimes attaches itself to potato starch, treatment of the crude starch with chlorine has been found satisfactory.[3] The M. Hansen process for potato starch manufacture,[4] is by bacterial fermentation in the absence of air. Methods of starch manufacture from potato peelings[5] and sweet potatoes[6] have been described. The relative tenacity of potato starch has been reported upon by G. Whewell[7] and W. Thomson.[8] The contributions of O. Saare[9] in this field

---

1. E. Snell, Dingl. Poly. 1844, **93,** 387. G. Vibrans, Zts. Spiritusind. 1883, 160. D. R. P. 57342, 1890. C. Weigelt, O. Saare and L. Schwab, Arch. f. Hygiene, 1885, III, 1. Dingl. Poly. 1843, **90,** 314. Zts. Spiritusind. 1885, 279; 1895, 294. L. Günther, Zts. Spiritusind. 1886, 248.

2. Zts. Spiritusind. 1892, 95; abst. J. S. C. I. 1893, **12,** 169. Zts. Spiritusind. 1894, 141.

3. C. Hellfrisch, E. P. 24456, 1895; abst. J. S. C. I. 1896, **15,** 284. C. Schaub, Bied. Centr. 1884, 285; abst. J. C. S. 1884, **46,** 1234. Mitth. ges. Starke. 1890, 37.

4. D. R. P. 281830, 1912; abst. J. S. C. I. 1915, **34,** 727; Chem. Zentr. 1915, **86,** II, 412; Chem. Ztg. Rep. 1915, **39,** 116; Zts. ang. Chem. 1915, **28,** 133.

5. E. Borras and Soc. Anon. Borras, E. P. 100675, 1916; abst. J. S. C. I. 1916, **35,** 860. E. P. 5099, 1915; abst. C. A. 1916, **10,** 2416, 2649. F. P. 478185, 1915; abst. J. S. C. I. 1916, **35,** 1126.

6. C. McDonnell, S. Carolina Exp. Sta. 1908, Bull. 136, 7; abst. J. S. C. I. 1909, **28,** 1265; C. A. 1908, **2,** 2464.

7. J. C. S. 1879, **36,** 570; Chem. News, 1879, **39,** 134.

8. Chem. News, 1879, **39,** 122.

9. Zts. Spiritusind. 1883, 174, 482, 543, 898, 1021, 1056; 1884, 18, 191, 216, 331, 550, 595, 762; 1885, 56, 156, 231, 240, 249, 454; 1886, 200, 476, 511, 519, 527; 1887, 2, 37, 41, 53, 60, 213, 296, 304, 320, 331; 1888, 6, 8, 13, 135, 144, 160, 301, 361, 377, 385, 391; 1889, 30, 33, 35, 137, 157, 306; 1890, 6, 13, 14, 15, 21, 59, 68, 89, 91, 102, 114, 119, 132, 147, 182, 189, 287, 295, 343, 352; 1891, 8, 11, 12, 15, 153, 237, 253, 259, 276, 291; 1892, 1, 10, 26, 34, 41, 42, 216, 311, 319, 327, 335, 343, 404, 550; 1893, 7, 50, 237, 269; 1894, 6, 8, 11, 13, 42, 49, 59; 1895, 13, 238, 349, 387, 405; 1897, Suppl. II, 4; 1898, **21,** 437; 1902, **25,** 44, 479; 1903, **26,** 436. Mitth. ges. Starke. 1890, 3, 5, 6, 15, 83, 104, 181, 182. J. S. C. I. 1884, **3,** 527; 1885, **4,** 236; 1897, **16,** 544, 623; 1899, **18,** 155, 1038; 1902, **21,** 265, 1401; 1903, **22,** 1153. Ann. Agron. **16,** 471; abst. J. C. S. 1891, **60,** 358. Dingl. Poly. 1885, **255,** 209; abst. J. C. S. 1885, **48,** 618.

have been extensive and varied, and covered a number of years.

Rice Starch. Although rice contains upwards of 80% of starch—an amount which surpasses that contained in any other raw material suitable for the preparation of starch,[1]—the cells and starch granules contained therein are so intimately associated by means of a thin but highly resistant layer of gluten, that the separation on a commercial scale cannot be effected by the simple processes which are used where potatoes or wheat is the raw farinaceous material.[2] On account of the smallness of the granules, rice starch possesses a firmness wanting in the other starches, so that in practical laundry and textile finishing operations a much higher luster is to be obtained with rice than by the use of the other starches. As soon as the difficulties in manufacture were understood and overcome, an impetus was given to its production in England, where at present it is carried on to a considerable extent.

The early method of manufacture as patented by O. Jones,[3] is with unimportant modifications, the process in use at the present day.[4] The rice is first softened in a dilute solution of sodium hydroxide for a 24 hour period of maceration, the mass being occasionally stirred. The liquor is decanted and the rice washed once or twice with fresh alkali water, allowed to drain, and then crushed or ground to flour between millstones. In France the softened rice is sometimes treated with an equal weight of 2% phosphoric acid to dissolve the gluten not acted upon by the alkali.[5] The flour thus obtained is again treated with caustic soda solution, being repeatedly agitated during 24 hours, and then left for a period of about 72 hours for the starch granules to settle. The portion first deposited comprises fibrous matter carrying but little starch, followed by a distinct layer of nearly all of

---

[1] M. Adlung. Deutsche Industrieztg. 1876, 142, 228; abst. Dingl. Poly. 1876, **221**, 58; J. C. S. 1876, **30**, 675; Industriebl. 1876, 173; Bayer, Ind. u. Gewerbebl. 1876, 142; Chem. Tech. Rep. 1876, **15**, I, 266; Jahr. Chem. 1876, **29**, 1136.

[2] M. Adlung, Dingl. Poly. 1876, **221**, 543; 1877, **224**, 304; abst. J. C. S. 1877, **32**, 363; Jahr. Chem. 1877, **30**, 1207; Wag. Jahr. 1876, **22**, 703.

[3] E. P. 8488, 1840.

[4] For general statement of progress in the manufacture of rice starch, see J. Hundhausen, Chem. Ztg. 1897, **21**, 777; Wag. Jahr. 1897, **43**, 781; Zts. Spiritusind. 1897. L. Hanemann, Chem. Ztg. 1897, **21**, 982; abst. J. S. C. I. 1898, **17**, 58.

[5] J. Jean & Co., F. P. 350370, 1904; abst. J. S. C. I. 1906, **25**, 191; Mon. Sci. 1906, **65**, 127; 1907, **67**, 44.

the starch, gluten and other insoluble material. The water is again run off, the starch stirred up with a large bulk of water, and after allowing the fibrous matter to subside while the starch is still in suspension (requiring about an hour), the aqueous portion with the major part of the starch still in suspension, is drawn off, passed through fine, silk sieves, and this process repeated several times, until the fibrous material is substantially removed from the starch granule.

In the process of W. Berger[1] the sodium hydroxide is replaced by sodium carbonate; in that of J. Colman,[2] rice is mixed with wheat refuse, the mass allowed to ferment for 10–15 days, after which the starch is separated by washing and sifting, as described above. H. Ransford[3] first submits the rice to the usual steeping operation, and then introduces a pressure of some 20 lbs. per sq. in. for the purpose of disintegrating the gluten and assisting in its removal. H. Kiel and R. Stoltenhoff[4] employ a vacuum for the same purpose. According to Leconte and Co.[5] best results are obtained by subjecting the starch in the steeping liquid to the action of an electric current which coagulates the impurities and gives the starch an unusual whiteness.[6] The manufacture of rice starch in Germany is given in detail in a series of articles by J. Berger.[7] In the method of H. Mack,[8] which has been used commercially in Germany, air under pressure is blown into the alkaline solution and rice, much of the impurities being carried away in the large amount of froth produced, and the rice, so it is claimed, is softened much quicker.

Y. Tanaka[9] has studied the hydrolysis of glutinous rice by diastase, and finds that the granules and products do not differ

---

[1] E. P. 9013, 1841.

[2] E. P. 9166, 1841.

[3] E. P. 603, 1853.

[4] E. P. 6778, 1888; abst. J. S. C. I. 1889, **8**, 298. See Rehe, E. P. 10359, 1884.

[5] U. S. P. 704349, 1902; abst. J. S. C. I. 1902, **21**, 1033. E. P. 2294, 1901; abst. J. S. C. I. 1902, **21**, 130. Aust. P. 7973, 1902.

[6] Societe des Produits Amylaces, Aust. P. 19613, 1905.

[7] Chem. Ztg. 1890, **14**, 1440, 1571; 1891, **15**, 843; abst. J. S. C. I. 1891, **10**, 152, 154, 781; Jahr. Chem. 1890, **43**, 2883; 1891, **44**, 2772.

[8] Dingl. Poly. 1885, **256**, 35. D. R. P. 30256, 1884; abst. Wag. Jahr. 1885, **31**, 657. Cf. C. Fehrmann, D. R. P. 29600; abst. Wag. Jahr. 1885, **31**, 659.

[9] J. Ind. Chem. 1912, **4**, 578; abst. J. S. C. I. 1912, **31**, 832; J. C. S. 1913, **104**, i, 446; 1912, **6**, 3035; Chem. Zentr. 1913, **84**, I, 309.

in appearance under the microscope from that of ordinary rice starch, nor does it contain Naegeli's amylodextrin, erythrodextrin or "albuminoids."[1] It probably contains a larger proportion of amylopectin than ordinary starch, or at least some analogous constituent yielding a dextrin hydrolyzed slowly by diastase.

According to E. Demoussy[2] rice starch demineralized by hydrochloric acid and washed until free from chlorides, exhibits properties of a weak acid comparable with carbonic acid and in this respect resembles some of the other carbohydrates.[3] It forms compounds with metallic hydroxides, ammonia and the alkali carbonates, which are dissociated by water. It is also capable of absorbing small quantities of neutral salts, i. e., sodium and potassium chlorides, potassium sulfate and copper acetate.

It has been found[4] that the ratio between starch and dextrose in pure rice starch is 93.2: 100. To trace out the cause of this discrepancy, Sostegni examined the insoluble residue obtained in the degradation of the starch molecule by unorganized ferments. A mixture of fatty acids was obtained containing a proportion of carbon less than that required for palmitic or oleic acid.

The influence of various salts at tenth-normal concentration on the rate of liquefaction of rice starch at 70° has been studied,[5] using the method of F. Warth and D. Darabsett. It has been claimed[6] that starches from different varieties of rice can be distinguished by fractional liquefaction at varying temperatures. In carrying out the test, one gram of material prepared in a state of fine subdivision by digestion with 1% KOH for 24 hours, is stirred with 70 cc. water and maintained at the desired tem-

---

[1] R. Atkinson, Chem. Sake. Brew. 1882, 2; Chem. News, 1881, **44**, 230; J. C. S. 1882, **42**, 432; Ber. 1881, **14**, 2287; Jahr. Chem. 1881, **34**, 985, 1308.

[2] Compt. rend. 1906, **142**, 933; abst. J. S. C. I. 1906, **25**, 489; abst., J. C. S. 1906, **90**, i, 401; J. S. C. I. 1906, **25**, 489; Rep. Chim. 1906, **6**, 312; Chem. Centr. 1906, **77**, I, 1654; Jahr. Chem. 1905–1908, II, 933.

[3] J. Ford and J. Guthrie, J. C. S. 1906, **89**, 76; Chem. News, 1905, **92**, 300; abst. J. S. C. I. 1906, **25**, 228; Bull. Soc. Chim. 1906, **36**, 1293; Chem. Centr. 1906, **77**, I, 314, 990; Jahr. Chem. 1905–1908, II, 923.

[4] L. Sostegni, Gazz. chim. ital. 1885, **15**, 376; abst. J. C. S. 1886, **50**, 221; 1888, **54**, 126; J. pharm. chim. 1886, **13**, 130; Ber. 1885, **19**, 103; Jahr. Chem. 1885, **38**, 1756.

[5] B. Viswanath, T. Row and P. Ayyangar, Mem. Dept. Agric. India, **6**, No. 5, 160; abst. J. S. C. I. 1916, **35**, 858; C. A. 1916, **10**, 2996.

[6] F. Warth and D. Darabsett, Mem. Dept. Agric. India, Chem. Series, 1914, **3**, 135; abst. J. S. C. I. 1914, **33**, 433; C. A. 1914, **8**, 2080.

perature for one hour. The starch liquefiable is converted into a paste, in which insoluble starch granules remain suspended. The cooled liquid is then treated for two hours with 10 cc. of malt extract at 30°, at which temperature no appreciable erosion of the starch granules occur. An aliquot portion of the filtered solution hydrolyzed with HCl, the dextrose determined by Fehling's solution; and a permanganate titration of the cuprous oxide; while the amount of starch liquefied at a given temperature is also ascertained. Characteristic curves for the various varieties of rice starch are obtained by plotting the percentage liquefaction against temperature.

Corn Starch. The manufacture of starch from corn (maize) is confined principally to the United States, where within the last twenty years it has developed to large proportions, and is controlled in a large measure by a single concern. Excellent articles on the details of this process have been given by G. Archbold[1] and more recently by W. Kaufmann,[2] the former giving details of the construction and operation of a plant of 1000 bushels per day capacity. The amount of starch in the corn used averages about 55% and is known as No. 4.[3]

In nearly all the processes of manufacture, advantage is taken of the fact that the kernel is surrounded by two distinct albuminoids, one of which is soluble in water, while the other requires a dilute alkali to cause it to pass into solution. Primarily, the process comprises the extraction of these nitrogenous bodies from the corn in such a manner that the starch, in passing through the various purification processes, is freed from those bodies liable to induce fermentation or acidification which tends to injuriously affect the final product.

The method generally employed is that known as the sulfur dioxide process, and consists first in steeping the whole grain in immense vats with about 1% aqueous sulfur dioxide at a tem-

---

1. J. S. C. I. 1887, **6**, 80, 189; 1902, **21**, 4; abst. Chem. Centr. 1887, **58**, 452; 1902, **73**, I, 605; Chem. Tech. Rep. 1887, **26**, II, 190; Rep. Chim. 1902, **2**, 214; Jahr. Chem. 1887, **40**, 2663; 1902, **55**, 1034; Wag. Jahr. 1887, **33**, 871; Zts. Chem. Ind. 1887, **1**, 263; **2**, 103.

2. J. S. C. I. 1910, **29**, 527; abst. Chem. Zentr. 1910, **81**, II, 250; Jahr. Chem. 1910, **63**, II, 412; Zts. ang. Chem. 1910, **23**, 2012.

3. The Manufacture of Corn Starch in the United States, J. Kriegner, Dingl. Poly. 1895, **295**, 39; abst. J. S. C. I. 1895, **14**, 287; Zts. Ver. Rübenzuckerind. 1893, 3; Chem. Centr. 1895, **66**, I, 565.

perature of about 130° F. for 2–4 days, the material meanwhile being kept in circulation. After draining, the softened corn is conveyed to the crushing mills, where it is decorticated and partially ground, then diluted with water and passed on to the degerminator. This is a long V-shaped tank, equipped with a screw conveyor at the bottom, and skimming arrangement at the top. The starch, endosperm and glutinous matter pass on, while the lighter oil-bearing sperm floats and is removed by the skimmer. This latter is cooked with live steam and hydraulically pressed, there exuding corn oil, and leaving an oil cake which is used as cattle food. The heavier than water portion is then screened by means of a vibrating copper sieve, the coarser material reground and re-treated as above, while the finer particles, either with or without being again treated, are run over a series of tables, runs or baffles where the starch separates and deposits by gravity, the glutinous and other impurities running away. The "green" starch which has been deposited in the tables is shoveled into the breakers—wooden vats provided with agitators—where water is introduced, and in which it is usual to introduce a small amount of caustic soda. After repeating the foregoing process, the now nearly purified product is run into settling tanks with a relatively large bulk of water, where, after subsidence, the water is withdrawn, the product washed several times with agitation, and finally dried in a manner previously described.

In the F. Baines process[1] the raw grain is first heated with 5–15 times its weight of water in a closed vessel at a temperature of 85°–95°. The J. Wildsmith method[2] is somewhat similar. The SO_2 process is due primarily to L. von Wagner.[3] W. Sage[4] precipitates the soluble products from the manufacture of corn starch by agitating the liquors with lime, transferring to a settling tank, drawing off the supernatant liquor, forcing the sediment into a press, and drying the pressed product.[5]

For the application of starch in the preparation of writing

---

[1] E. P. 18258, 1891. S. Bensaude uses manioc roots for starch production in E. P. 15896, 1886.

[2] E. P. 4146, 1883.

[3] E. P. 4758, 1886; abst. J. S. C. I. 1886, **5**, 330. Dingl. Poly. 1884, **250**, 173; J. C. S. 1884, **46**, 528; J. S. C. I. 1884, **3**, 323. See also L. von Wagner, Handbuch der Stärkefabrikation, Weimar, 1875.

[4] U. S. P. 1187392, 1916; abst. J. S. C. I. 1916, **35**, 858; C. A. 1916, **10**, 2160.

[5] Anon. Dingl. Poly. 1880, **238**, 488; abst. J. C. S. 1881, **40**, 330. A. Riche, J. pharm. chim. 1880, **1**, 137; Chem. Tech. Rep. 1880, **19**, I, 233.

papers, consult H. Wrede[1] who has made exhaustive experiments.

Action of Diastatic Ferments on Starch. It has been known for a long time that certain enzymes exert a most powerful action on gelatinized starch as well as on some varieties of starch in the raw or natural state. Of these ferments, in point of activity is the diastase of malted barley, in addition to the saliva and pancreatic juice mentioned in a preceding topic.

In general, if the action of a solution of any one of these ferments on starch paste be observed, the first effect is complete liquefaction with the almost immediate formation of a limpid liquid. The iodine test applied at this point will show the presence of soluble starch. The next stage in the process is the saccharification of the soluble starch. This is indicated by the disappearance of the blue color first produced by the iodine, giving place to a reddish brown color indicating the presence of erythro-dextrin, which in turn is transformed into acroodextrin. Coincidentally with the disappearance of the starch is observable the appearance of sugars in an analogous ratio.

Diastase does not act upon non-gelatinized starch in the cold,[2] a statement which Kjeldahl holds does not apply to all the starches. According to C. O'Sullivan,[3] this is probably due to some condition of the starch connected with the degree of ripeness of the material from which it was obtained. The action and the products of diastase on starch paste has been the subject of repeated investigation, but as yet the periphery of the subject has apparently been but touched.

According to A. Fernbach and J. Wolff,[4] extracts of barley convert the most resistant dextrins into maltose; the change being much slower than with malt extract. When the temperature is raised to 45° the action is incomplete and a residue of a stable

[1] Wochenbl. Papierfabr. 1912, **43**, 1004; Zts. Spiritusind. 1913, **36**, 467; J. S. C. I. 1912, **31**, 381; 1913, **32**, 974; C. A. 1912, **6**, 2526; 1913, **7**, 2114.

[2] H. Brown and J. Heron, J. C. S. 1879, **35**, 596; Chem. News, 1879, **39**, 284; 1880, **41**, 22; abst. Ann. 1879, **199**, 165; Ber. 1879, **12**, 1477; Jahr. Chem. 1879, **32**, 838; Jahr. rein Chem. 1879, **7**, 507.

[3] J. C. S. 1876, **29**, 478; 1876, **30**, 133; Chem. News, 1876, **33**, 218; abst. Bull. Soc. Chim. 1877, **27**, 81; Ber. 1876, **9**, 650, 949; Chem. Centr. 1876, **47**, 564; Jahr. Chem. 1876, **29**, 837, 838, 1147; Wag. Jahr. 1876, **22**, 717; Bayer. Bierbrauer, 1876, 91; Mon. Sci. 1876, **18**, 1218.

[4] Compt. rend. 1907, **145**, 80, 261; abst. J. C. S. 1907, **92**, i, 750; C. A. 1907, **1**, 2419, 2498; J. S. C. I. 1907, **26**, 833; Biochem. Centr. 1907, **6**, 537, 800; Chem. Zentr. 1907, **78**, II, 614, 997; Jahr. Chem. 1905–1908, II, 924, 943, 4670.

dextrin remains. Moreover[1] the diastatic liquefaction of starch is subject to the same influences as liquefaction under pressure.[2] This is corroborated by the work of Z. Wierzchowski,[3] A. Schifferer[4] and E. v. Sigmond.[5] M. Pauletig[6] has incubated solutions of the various starches with diastase from different sources and draws the conclusion that diastase hydrolyzes starch from cereals more readily than starch from the Leguminosae. S. Kende has found[7] that the soaps of the higher fatty acids inhibit the degradsion by diastase of starch and glycogen, the action differing from the ordinary action of ferment inhibitors in that the soap does not act directly on the enzyme, but on the substance with which it forms apparently an adsorption compound.[8]

When diastase from ungerminated barley acts at 50° on a solution of soluble starch, hydrolysis proceeds until at the end

[1] Ann. Inst. Pasteur, 1904, **18**, 165; abst. J. C. S. 1904, **86**, i, 374; J. S. C. I. 1904, **23**, 449; Rep. Chim. 1904, **4**, 131, 125; Chem. Centr. 1904, **75**, II, 47; Jahr. Chem. 1904, **57**, 2134. Compt. rend. 1907, **145**, 261, 263; abst. J. C. S. 1907, **92**, i, 1012. A. Fernbach and M. Schoen, Bull. Soc. Chim. 1912, **11**, 303; abst. J. C. S. 1912, **102**, i, 336; J. S. C. I. 1912, **31**,-402.

[2] J. Ford, J. S. C. I. 1904, **23**, 414; abst. J. C. S. 1904, **85**, 980; 1904, **86**, ii, 452; Chem. News, 1904, **89**, 247; Rep. Chim. 1904, **4**, 462; Chem. Centr. 1904, **75**, II, 645, 825; Jahr. Chem. 1904, **57**, 1152, 2125.

[3] Biochem. Zts. 1913, **56**, 209; abst. J. C. S. 1913, **104**, i, 1255; C. A. 1914, **8**, 1028; J. S. C. I. 1913, **32**, 1026; Chem. Zentr. 1913, **84**, II, 2142.

[4] Inaug. Dissertation, Keil, 1892; abst. Neue. Zts. Rüb. Zuck. Ind. 1892, **29**, 167; J. S. C. I. 1893, **12**, 368; Jahr. Chem. 1892, **45**, 2842; Zts. Spiritusind. 1892, 313, 345; Pharm Centralh. 1893, 507; J. C. S. 1893, **64**, i, 127; Chem. Centr. 1892, **63**, II, 339; Chem. Tech. Rep. 1893, **32**, II, 105; Chem. Ztg. Rep. 1892, **16**, 336; Meyer Jahr. Chem. 1892, **2**, 403; Tech. Chem. Jahr. 1892–1893, **15**, 301; Wag. Jahr. 1892, **38**, 874.

[5] Wochensch. f. Brau. 1897, **14**, 412; abst. J. S. C. I. 1897, **16**, 817; J. C. S. 1898, **74**, i, 398; Zts. Spiritusind. 1897, **20**, 261; Chem. Centr. 1897, **68**, II, 614; Chem. Tech. Rep. 1897, **36**, 531; Jahr. Chem. 1897, **50**, 1520; Tech. Chem. Jahr. 1897–1898, **20**, 260; Wag. Jahr. 1897, **43**, 791, 928.

[6] Zts. physiol. Chem. 1917, **100**, 74, abst. J. C. S. 1917, **112**, i, 670; C. A. 1918, **12**, 159.

[7] Biochem. Zts. 1917, **82**, 30; abst. J. C. S. 1917, **112**, i, 615.

[8] V. Koudeka, Allgem. Zts. Bierbrau u Malz fabr. 1916, **44**, 71; Zts. ges. Brauw. 1916, **39**, 222; J. S. C. I. 1917, **36**, 399. G. Krabbe, Pringsheim's Jahr. wiss. Bot. 1890, **21**, 520; abst. Bied. Centr. **20**, 61; J. C. S. 1891, **60**, 605; 1892, **62**, 92; Jahr. Chem. 1891, **44**, 2739; Chem. Tech. Rep. 1890, **29**, I, 79. C. Krötke, Dingl. Poly. 1872, **204**, 241; abst. J. C. S. 1872, **25**, 937; Chem. Tech. Rep. 1871, **10**, I, 101; Jahr. Chem. 1872, **25**, 1022. P. Lindner, Zts. ges. Brauw. 1907, **30**, 109; Wochenschr. Brau. 1907, **24**, 278; Chem. Zentr. 1907, **78**, II, 169; J. S. C. I. 1907, **26**, 706. A. Ling, Brit. Assoc. Report, 1903, advance sheet; abst. J. S. C. I. 1903, **22**, 1058. J. Fed. Inst. Brewing, 1903, **9**, 446; abst. J. S. C. I. 1903, **22**, 1204; J. C. S. 1904, **86**, i, 558. Seventh Internl. Cong. Appl. Chem. 1909; abst. J. S. C. I. 1909, **28**, 731. J. Int. Brew. 1911, **17**, 570; abst. J. S. C. I. 1911, **30**, 1328. A. Ling and J. Baker, Proc. Chem. Soc. 1895, 3; abst. J. S. C. I. 1895, **14**, 175. F. v. Mering, Zts. Phys. Chem. 1881, **5**, 185; abst. J. C. S. 1882, **42**, 749; Chem.

of 1–1.5 hours maltose, unaltered dextrin and glucose are formed.[1]

F. Musculus states[2] that when diastase dissolves starch paste at 70°–75°, the product consists of one molecule of sugar and two molecules of dextrin, and that when the reaction reaches this

---

Tech. Rep. 1881, **20**, 1, 30; Zts. d. Spiritusfabr. 1881, 206. T. Moreau, Ann. Soc. Roy. med. et mat. **64**; abst. Woch. f. Brau. 1905, **22**, 37, 49, 72; J. S. C. I. 1905; **24**, 204.

[1] J. Baker, J. C. S. 1902, **82**, 1177; abst. J. S. C. I. 1902, **21**, 1087. J. Baker and H. Hulton, Chem. Soc. Trans. 1914, **105**, 1529; abst. J. S. C. I. 1914, **23**, 760. Analyst, 1917, **42**, 351. J. Wolff, J. prakt. Chem. 1857, **71**, 86; Dingl. Poly. 1857, **145**, 451. Compt. rend. 1905, **141**, 1046; abst. J. C. S. 1906, **92**, i, 66. Ann. Chim. Anal. 1905, **10**, 389; abst. J. C. S. 1905, **88**, ii, 866; 1906, **90**, ii, 500; Woch. f. Brau. 1906, **23**, 31, 316; J. S. C. I. 1906, **25**, 139, 716; Ann. de la Brasserie, 1907; Wochenbl. Brauer, 1908, 27. F. P. 360091, 1905; abst. J. S. C. I. 1906, **25**, 437. J. Wolff and A. Fernbach, Compt. rend. 1903, **137**, 718; abst. J. S. C. I. 1903, **22**, 1302; J. C. S. 1904, **86**, i, 211. Compt. rend. 1904, **138**, 49, 818; **139**, 1217. Compt. rend. 1905, **140**, 1403; abst. J. C. S. 1905, **88**, i, 510. Compt. rend. 1906, **143**, 363; abst. J. C. S. 1906, **90**, i, 803. Compt. rend. 1907, **144**, 645; abst. J. C. S. 1907, **92**, i, 482. J. Wolff and E. Roux, Compt. rend. 1905, **141**, 1046; abst. J. S. C. I. 1906, **25**, 34. C. Lintner, J. prakt. Chem. 1886, **34**, 378; 1887, **36**, 481; 1890, **41**, 91. Zts. ang. Chem. 1888, **1**, 232; 1890, **3**, 546; abst. J. C. S. 1889, **56**, 316; 1891, **60**, 537. Brauer and Mälzerkalender, **13**, 83; abst. J. S. C. I. 1890, **19**, 402. Wochenschr. f. Brauer, **9**, 245; abst. Jahr. Chem. 1892, **45**, 2465; Zts. ang. Chem. 1892, **5**, 263; Chem. Centr. 1892, **63**, I, 623. Zts. ges. Brauw. 1892, **15**, 123; abst. J. S. C. I. 1892, **11**, 1021. Ber. 1895, **28**, 1522. Chem. Zts. 1897, **21**, 737, 752; abst. J. S. C. I. 1897, **16**, 1028. Zts. ang. 1898, **11**, 725; abst. J. S. C. I. 1898, **17**, 878. Zts. Nahr. Genussm. 1907, **14**, 205; 1908, **16**, 509; abst. J. C. S. 1907, **92**, ii, 823; 1908, **94**, ii, 1077. Zts. ges. Brauw. 1907, **30**, 109; abst. J. S. C. I. 1907, **26**, 281. Zts. ang. Chem. 1912, **25**, 1177; abst. J. S. C. I. 1912, **31**, 653. C. Lintner and G. Düll, Zts. ang. Chem. 1891, **4**, 537. Zts. ges. Brauw. 1892, **15**, 145; abst. Zts. ang. Chem. 1892, **5**, 263; Chem. Centr. 1892, **63**, 263; Jahr. Chem. 1892, **45**, 2464. Chem. Ztg. 1893, **17**, 1340; abst. J. C. S. 1894, **66**, i, 5; J. S. C. I. 1894, **13**, 53; Bull. Soc. Chim. 1894, **12**, 439; Ber. 1893, **26**, 2531; Chem. Centr. 1894, **65**, I, 22; Jahr. Chem. 1893, **46**, 891. Zts. ges. Brauw. **17**, 339; abst. Jahr. Chem. 1894, **47**, 1140. Zts. f. ges. Br. 1895, **18**, 153. M. Baswitz, Ber. 1878, **11**, 1443; 1879, **12**, 1831; abst. J. C. S. 1878, **34**, 903; 1880, **38**, 132; Jahr. Chem. 1878, **31**, 1034, 1155; 1879, **32**, 836; Chem. Tech. Rep. 1878, **17**, II, 60. M. Battegay, Färber. Ztg. 1912, **23**, 133; abst. J. S. C. I. 1912, **31**, 427; C. A. 1913, **7**, 1794; Chem. Zentr. 1912, **83**, I, 1934. W. Biltz, Ber. 1913, **46**, 1532; abst. J. S. C. I. 1913, **32**, 619; J. C. S. 1913, **104**, i, 707; C. A. 1913, **7**, 2702; Chem. Zentr. 1913, **84**, II, 31. A. Board and A. Ling, E. P. 19391, 1909; abst. J. S. C. I. 1910, **29**, 1174; C. A. 1911, **5**, 2299. F. Braunbeck, E. P. 25595, 1906; abst. J. S. C. I. 1907, **26**, 984; C. A. 1907, **1**, 2647. A. Bryant and C. Miner, Eighth Inter. Cong. Appl. Chem. 1912, **13**, 57; J. C. S. 1913, **104**, i, 832; C. A. 1912, **6**, 3035.

[2] Ann. Chim. Phys. 1860, (3), **60**, 203; Compt. rend. 1860, **50**, 785; abst. Chem. News, 1860, **1**, 287; Mon. Sci. 1859–1860, **2**, 710; J. pharm. chim. 1860, **37**, 419; Rep. Chim. appl. 1860, **2**, 140; Instit. 1860, 147; Chem. Centr. 1860, **31**, 602; Dingl. Poly. 1860, **158**, 424; Jahr. Chem. 1860, **13**, 502; Wag. Jahr. 1860, **6**, 335; Zts. Chem. 1860, **3**, 379. Compt. rend. 1862, **54**, 194; abst. Rep. Chim. Pure, 1862, **4**, 148; Dingl. Poly. 1862, **164**, 150; Jahr. Chem. 1861, **14**, 148; Zts. Chem. 1862, **5**, 169.

stage no further action takes place. A. Payen asserts[1] that more than 50% of the solid matter dissolved by the reaction is sugar, and affirms[2] that four samples taken from an operation in the space of 4.5 hours contained 8% to 26% of sugar on the total solids dissolved.[3] Schwarzer[4] agrees with F. Musculus[5] and F. Musculus and D. Gruber[6] in finding equivalent amounts of dextrin and sugar in solution, but differs from him in supposing that dextrin is first formed and then sugar, and that the action ceases when definite equivalent proportions are produced. He maintains less sugar is formed at 65° than at lower temperatures.

[1] Ann. Chim. Phys. 1865, (4), **4**, 286; abst. Chem. News, 1865, **11**, 209; Bull. Soc. Chim. 1865, **3**, 470; J. pharm. chim. 1865, **1**, 363; Chem. Centr. 1865, **36**, 845; Dingl. Poly. 1865, **178**, 69; Jahr. Chem. 1865, **18**, 597; Vierteljahrsch. pr. Pharm. **25**, 221.

[2] Ann. Chim. Phys. 1866, **7**, 382; abst. Jahr. Chem. 1866, **19**, 662; Zts. Chem. 1866, **9**, 334.

[3] L. Cuisinier, U. S. P. 311646, 1885. E. P. 14271, 1884; 7788, 1885; 1820, 1886. D. R. P. 37923, abst. J. C. S. 1887, **52**, 354; J. S. C. I. 1885, **4**, 237; 1886, **5**, 331; 1887, **6**, 375; Mon. Sci. 1886, **28**, 840; Ber. 1887, **20**, R, 128; Chem. Centr. 1886, **57**, 614; 1887, **58**, 292; Chem. Ind. 1887, **10**, 322; Chem. Tech. Rep. 1886, **25**, I, 44; 1887, **26**, I, 77, 172; II, 103, 194; Chem. Ztg. Rep. 1886, **10**, 35; 1887, **11**, 214; Dingl. Poly. 1887, **65**, 325; Jahr. Chem. 1887, **40**, 2660; 1888, **41**, 2807; Wag. Jahr. 1886, **32**, 611; Rev. Brass. 1887, No. 651; Zts. Spiritusind. 1887, **10**, 223; 679, N. Zts. Rübenzuckerind. 1886, **16**, 32. H. Pottevin, Compt. rend. 1898, **126**, 1218; abst. J. S. C. I. 1898, **17**, 590. Ann. Inst. Pasteur, **13**, 665; abst. Chem. Centr. 1899, **70**, II, 644; J. S. C. I. 1899, **18**, 1145. Woch. f. Brau. 1899, **16**, (48), 641; abst. J. S. C. I. 1900, **19**, 162. S. Pratt, U. S. P. 524651, 1894. E. P. 3302, 1893; abst. J. S. C. I. 1893, **12**, 940. H. Brown, G. Morris and E. Moritz, E. P. 1809, 1890; abst. J. S. C. I. 1891, **10**, 265. H. van Laer, J. Fed. Inst. Brew. 1900, **6**, (3), 162; abst. J. S. C. I. 1900, **19**, 457. Bull. Soc. Chim. Belg. 1907, **21**, 8; 1911, **25**, 249, 393; 1912, **26**, 18; abst. J. S. C. I. 1907, **26**, 161; 1911, **30**, 1024, 1465; 1912, **31**, 197; J. C. S. 1912, **102**, ii, 35. Bull. Acad. Roy. Belg. 1910, 611, 707; 1911, 795; abst. J. C. S. 1910, **98**, ii, 839; 1911, **100**, ii, 28, 478; 1912, **102**, ii, 148; J. S. C. I. 1912, **31**, 245; Chem. Zentr. 1912, **83**, I, 483. A. Fernbach and J. Wolff, Compt. rend. 1906, **142**, 1216; abst. J. S. C. I. 1906, **25**, 648; J. C. S. 1906, **90**, i, 484; Chem. Centr. 1906, **75**, II, 229; Chem. Zts. 1907, **6**, 266; Jahr. Chem, 1905–1908, II, 924.

[4] J. prakt. Chem. 1870, **109**, 212; abst. Chem. News, 1870, **23**, 22; Bull. Soc. Chim. 1870, **14**, 400; Chem. Centr. 1870, **41**, 295; Industriebl. 1870, 154; Chem. Tech. Rep. 1870, **9**, I, 36; Dingl. Poly. 1870, **198**, 321; Jahr. Chem. 1870, **23**, 854; Wag. Jahr. 1870, **16**, 447; Bayer. Bierbrauer, 1870, 128; Poly. Notizbl. 1870, **25**, 321; Poly. Centr. 1870, **36**, 844.

[5] Ann. Chim. Phys. 1860, (3), **60**, 202. Compt. rend. 1860, **50**, 785; 1862, **54**, 194; 1869, **68**, 1267; 1870, **70**, 857; 1874, **78**, 1413; 1879, **88**, 612; abst. J. C. S. 1879, **36**, ii, 518; Bot. Ztg. 1879, No. 22, 345. Bied. Centr. 1881, 355; abst. J. C. S. 1881, **40**, 888. J. prakt. Chem. 1883, **136**, 496; abst. J. C. S. 1884, **46**, 574. Ann. Chim. Phys. 1885, (6), **4**, 177. Ber. 1892, **25**, 519. F. Musculus and J. de Mering, Bull. Soc. Chim. 1879, **31**, 105; abst. J. C. S. 1879, **36**, 370. Zts. Phys. Chem. 1881, **5**, 122.

[6] Compt. rend. 1878, **86**, 1459; abst. J. C. S. 1878, **34**, 778. Bull. Soc. Chim. 1878, **30**, 54; Ber. 1879, **12**, 287; Jahr. Chem. 1878, **31**, 924.

C. O'Sullivan[1] demonstrated that the sugar so produced was not dextrose but maltose, and that the methods used in estimating the dextrose was wrong. He has also shown that dextrose and maltose are the invariable products of the transformation, and that by continuing the action, the whole of the dextrin can be converted into maltose.

F. Musculus states[2] that the saccharification of starch paste with diastase ceases when half the matter in solution is sugar. He attributes his original impression that but one-third was converted into sugar to the varying structure of the starch granules, the coating of one variety offering a greater resistance to the action of the diastase than that of another. L. Bondonneau holds[3] that the action is not a splitting-up of the starch aggregate, but that the starch molecule passes through the following four modifications: amylogen, α-dextrin, β-dextrin and γ-dextrin, before it arrives at the end-product, glucose. A. Petit[4] mentions the presence of a fermentable sugar soluble in alcohol as a constituent of the transformation products, and without action upon Fehling's solution.

C. O'Sullivan[5] has apparently conclusively proven when working under clearly defined conditions, that maltose and dextrin are the only products of the action, although he pointed out the presence of a body which gave a reduction with copper oxide equivalent to 9%–10% of dextrose.[6] He also has shown that solu-

---

1. J. C. S. 1872, **25**, 581; 1876, **30**, 137; abst. Chem. News, 1876, **33**, 218; Bull. Soc. Chim. 1877, **27**, 81; Mon. Sci. 1876, **18**, 1218; Ber. 1876, **9**, 650, 949; Chem. Centr. 1876, **47**, 564; Jahr. Chem. 1876, **29**, 837, 838, 1147; Wag. Jahr. 1876, **22**, 717; Bayer. Bierbrauer, 1876, 91.

2. Bull. Soc. Chim. 1874, **22**, 32; abst. Chem. News, 1874, **30**, 20; J. C. S. 1874, **27**, 1077, 1174; J. pharm. chim. 1874, **20**, 39; Ber. 1874, **7**, R, 824; Chem. Tech. Rep. 1874, **13**, II, 152; Jahr. Chem. 1874, **27**, 881.

3. Compt. rend. 1875, **81**, 1212; abst. Chem. News, 1875, **32**, 281; **33**, 18; J. C. S. 1876, **29**, 365; Bull. Soc. Chim. 1876, **25**, 2; J. pharm. chim. 1876, **23**, 34; Ber. 1876, **9**, 61, 69; Jahr. Chem. 1875, **28**, 789.

4. Bull. Soc. Chim. 1875, **24**, 519; abst. Chem. News, 1876, **33**, 10; Ber. 1875, **8**, 1595; Chem. Tech. Rep. 1875, **14**, II, 82; Jahr. Chem. 1875, **28**, 788.

5. J. C. S. 1876, **30**, 125; 1879, **35**, 770; abst. Chem. News, 1876, **33**, 218; 1879, **40**, 236, 288; Bull. Soc. Chim. 1877, **27**, 81; 1879, **32**, 492; Ber. 1876, **9**, 650, 949; Chem. Centr. 1876, **47**, 564; Wag. Jahr. 1876, **22**, 717; Bayer Bierbrauer, 1876, 91; Jahr. Chem. 1876, **29**, 837, 841, 1147; 1879, **32**, 845.

5. A. Lebedeff, Biochem. Zts. 1908, **9**, 392; abst. J. C. S. 1908, **94**, i, 321; C. A. 1909, **3**, 188; Bull. Soc. Chim. 1908, **4**, 1575; Chem. Zentr. 1908, **79**, I, 1712. J. Ford, J. S. C. 1904, **85**, 980; 1905, **86**, ii, 452; J. S. C. I. 1904, **23**, 414, 875; abst. Chem. News, 1904, **89**, 247; Rep. Chem. 1904, **4**, 462;

ble starch is the first product of the action,[1] and has concluded that it is possible only one dextrin exists.

F. Musculus and D. Gruber[2] regard starch as a polysaccharide containing at least five times the group $C_{12}H_{20}O_{10}$, and when this is acted upon by diastase or dilute acids it is broken down with hydration into maltose, and a dextrin containing a $C_{12}H_{20}O_{10}$ group less than starch; furthermore, that this dextrin is broken down in the same manner, maltose and a dextrin containing a $C_{12}H_{20}O_{10}$ group less than the previous one, and so on through a series until finally the solution contains only maltose.

M. Maerker[3] believes that at 60° four molecules of starch yield three molecules of maltose and one of dextrin, while at 65° less maltose is formed. H. Brown and J. Heron[4] have eliminated out of the possible varying proportions of maltose and dextrin indicated by C. O'Sullivan, eleven distinct transformation products. It is the judgment of A. Herzfeld[5] that erythro- and acroo-dextrins are without reducing power on copper solution, and calls attention to the presence of a substance among the transformation products which appears to hold a position between dextrin and maltose, and which he proposes the name malto-dextrin. While H. Brown and G. Morris[6] confirm the presence

Chem. Centr. 1904, **75**, II, 645, 825; Jahr. Chem. 1904, **57**, 1152, 2125. Analyst, 1904, **29**, 277; abst. J. S. C. I. 1904, **23**, 414, 953. J. Ford and J. Guthrie, J. S. C. I. 1905, **24**, 605; abst. Chem. Centr. 1905, **76**, II, 544; Jahr. Chem. 1905–8, II, 942; Meyer Jahr. Chem. 1905, **15**, 410. S. Vines, Brit. Assoc. Reports, 1891, 697; Annals of Botany, 1891, 409.

[1] O'Sullivan, J. C. S. 1879, **35**, 770; abst. Chem. News, 1879, **40**, 236, 288; Bull. Soc. Chim. 1879, **32**, 493; Jahr. Chem. 1879, **32**, 845.

[2] Bull. Soc. Chim. 1878, **30**, 54; Compt. rend. 1878, **86**, 1459; abst. J. C. S. 1878, **34**, 778; Ber. 1879, **12**, 287; Jahr. Chem. 1878, **31**, 924.

[3] Landw. Vers.-Stat. **23**, 69; Munich Naturforscher Vers. 1877, 222; abst. J. C. S. 1878, **34**, 969; Ber. 1877, **10**, 2234; Chem. Centr. 1878, **49**, 559; Jahr. Chem. 1877, **30**, 900; 1878, **31**, 1035.

[4] J. C. S. 1879, **35**, 596; abst. Chem. News, 1879, **39**, 284; 1880, **41**, 22; Ann. 1879, **199**, 165; Ber. 1879, **12**, 1477; Jahr. Chem. 1879, **32**, 838; Jahr. rein Chem. 1879, **7**, 507.

[5] Ber. 1879, **12**, 2120; 1885, **18**, 3469; abst. Chem. News, 1880, **41**, 92; **42**, 96; 1883, **48**, 194; J. C. S. 1880, **38**, 310, 866; 1881, **40**, 1024; 1886, **50**, 221; Bull. Soc. Chim. 1880, **34**, 538; Chem. Tech. Rep. 1879, **18**, II, 74; 1880, **19**, I, 232; Jahr. Chem. 1879, **32**, 837; 1885, **38**, 1758.

[6] J. C. S. 1885, **47**, 527; 1889, **55**, 449; 1890, **57**, 458, 489; 1895, **67**, 309; abst. Chem. News, 1885, **51**, 308; 1886, **53**, 37; 1889, **59**, 295; 1890, **61**, 201; 1895, **71**, 123; Bull. Soc. Chim. 1890, **4**, 682; 1891, **5**, 543; 1896, **16**, 1006; J. S. C. I. 1885, **4**, 682; 1889, **8**, 716; 1895, **14**, 288. Ber. 1885, **18**, R, 615; 1889, **22**, R, 740; 1890, **23**, R, 502; 1895, **28**, R, 642; Chem. Centr. 1889, **60**, II, 124, 285; 1890, **61**, I, 1006; II, 149; 1895, **66**, I, 849; Ann. 1885, **231**, 72,109, 125; Jahr. Chem. 1885, **38**, 1757; 1889, **42**, 136, 2063; 1890, **43**, 2174; 1895, **48**, 1335.

of malto-dextrin, but find that the physical constants point to it as a mixture of maltose and dextrin. They conclude[1] that the dextrins are metameric rather than polymeric.

A new angle to this subject has been brought out by C. Lintner and G. Düll,[2] who have isolated a body which they term isomaltose, which is less fermentable and soluble in alcohol than maltose, and which is completely transformed into maltose by diastase. G. Morris and J. Wells,[3] and E. Moritz[4] have subsequently described a whole series of amyloins or malto-dextrins among which they describe as restricted starch conversions, and assert that isomaltose is an amyloin in which the maltose portion largely predominates. The above statements are contended by A. Schifferer.[5]

It has been found by A. Fernbach and J. Wolff[6] that at a temperature of 50°, starch is almost completely converted into maltose by the action of malt extract, while the second phase of the reaction, i. e., the transformation of the dextrin into maltose is accelerated by the addition of acid until the liquid is neutral to methyl orange. These statements are corroborated by L. Brasse.[7]

L. Maquenne and E. Roux[8] hold that the optimum reaction

---

[1] J. C. S. 1889, **55**, 462.

[2] Zts. ang. Chem. 1892, **5**, 263; Zts. ges. Brauw. 1892, **15**, 145; abst. J. C. S. 1893, **64**, i, 51; J. S. C. I. 1892, **11**, 766, 1021; Ber. 1892, **25**, R, 576; Chem. Centr. 1892, **63**, I, 886; Jahr. Chem. 1892, **45**, 2464.

[3] Trans. Inst. Brew. 1892, **5**, 133; abst. J. C. S. 1894, **66**, i. 223; Chem. Centr. 1892, **63**, II, 222; Tech. Chem. Jahr. 1892–1893, **15**, 306; Wag. Jahr. 1892, **38**, 887; Wochenschr. f. Brauerei, 1892, 886; Zts. ges. Brauw. 1892, 419.

[4] Trans. Inst. Brew. 1891, **4**, 141; abst. Zts. ges. Brauw. 1891, **14**, 199, 222; Chem Centr. 1891, **62**, I, 324; Wag. Jahr. 1891, **37**, 974; Tech. Chem. Jahr. 1891–1892, **14**, 260; Jahr. Chem. 1891, **44**, 2765.

[5] Inaug. Dissertation, Basel.

[6] Compt. rend. 1906, **142**, 1216; abst. J. C. S. 1906, **90**, i, 484; J. S. C. I. 1906, **25**, 648; Chem. Centr. 1906, **75**, II, 229; Chem. Zts. 1907, **6**, 266; Jahr. Chem. 1905–1908, II, 924.

[7] Compt. rend. 1884, **99**, 878; 1885, **100**, 454; abst. J. C. S. 1885, **48**, 499. Ann. Agronom. **12**, 200; abst. J. C. S. 1886, **50**, 827.

[8] Compt. rend. 1905, **140**, 1303; abst. Chem. News, 1905, **91**, 279; J. C. S. 1905, **88**, i, 511; J. S. C. I. 1905, **24**, 630; Bull. Soc. Chim. 1905, **33**, 723; Rep. Chim. 1905, **5**, 318; Chem. Centr. 1905, **76**, II, 121, 314; Chem. Zts. 1906, **5**, 10; Meyer Jahr. Chem. 1910, **15**, 410; Biochem. Centr. 1905–1906, **4**, 138, 380; Tech. Chem. Jahr. 1905, **28**, 274. Compt. rend. 1906, **142**, 124, 1059; abst. J. C. S. 1906, **90**, i, 327, 547; J. S. C. I. 1906, **25**, 192; Ann. Chim. Phys. 1906, (8), **9**, 179; Rep. Chim. 1906, **6**, 174; Chem. Zts. 1907, **6**, 266; Jahr. Chem. 1905–1908, II, 4670; Wag. Jahr. 1906, **52**, II, 225. L. Maquenne, Compt. rend. 1903, **137**, 85, 658, 797, 1266; abst. J. C. S.

at which amylase acts on various kinds of starch is that of exact neutrality. Starch solutions, and solutions of amylase from malt are usually alkaline, so that sufficient mineral acid must be added for exact neutralization. E. Fouard[1] and A. Reychler[2] in the main agree that the action of bases upon starch appears to be to disintegrate the complex starch molecules with the formation of a simple $C_6H_{10}O_5$ group, which then reacts with the base, so that in the reversible reaction, disintegration and re-formation of complex molecules occur.[3]

The conversion of starch by diastase is hastened by the presence of carbon dioxide and citric acids, and retarded by the

---

1903, **84**, i, 679; 1904, **86**, i, 17, 18, 227, 800; Bull. Soc. Chim. 1903, **29**, 1218; Rep. Chim. 1904, **4**, 57, 102, 131, 177; Chem. Centr. 1903, **74**, II, 757; 1904, **75**, I, 361, 467; Chem. Zts. 1903–1904, **3**, 642; Jahr. Chem. 1903, **56**, 1005; Wag. Jahr. 1904, **50**, II, 224; Chem. News, 1903, **87**, 90; 1903, **88**, 269, 305. 1904, **89**, 59, 101; L. Maquenne, A. Fernbach and J. Wolff, Compt. rend. 1904, **138**, 49; abst. J. C. S. 1904, **86**, i, 228.

[1] Bull. Soc. Chim. Belg. 1910, **24**, 105; abst. J. C. S. 1910, **98**, i, 225; C. A. 1910, **4**, 2104; Chem. Zentr. 1910, **81**, I, 1006. Cf. Compt. rend. 1908, **147**, 931; **148**, 502; abst. C. A. 1910, **4**, 842; J. C. S. 1909, **96**, i, 13, 209, 699; Bull. Soc. Chim. 1909, **5**, 828; Chem. Zentr. 1909, **80**, I, 68, 644, 1091, 1987; II, 974.

[2] Bull. Soc. Chim. Belg. 1909, **23**, 378; abst. J. C. S. 1909, **96**, ii, 977; C. A. 1910, **4**, 270; J. S. C. I. 1909, **30**, 1216; Chem. Zentr. 1909, **80**, II, 2140.

[3] B. Viswanath, T. Row and P. Ayyangar, Mem. Dept. Agric. India, Chem. Series, **4**, No. 5, 160; abst. J. S. C. I. 1916, **35**, 858; C. A. 1916, **10**, 2996. C. Scheibler, Zts. anal. Chem. 1869, **8**, 473; Ber. 1869, **2**, 170; abst. Ann. Landw. 1869, 182; Deut. Indztg. 1869, 203; Ind. u. Gewerbebl. 1869, 181; Chem. News, 1869, **19**, 297; Bull. Soc. Chim. 1869, **13**, 92; Poly. Centr. 1869, **35**, 749; Poly. Notizbl. 1869, **24**, 338; Dingl. Poly. 1869, **192**, 504; Jahr. Chem. 1869, **22**, 949; Wag. Jahr. 1869, **15**, 387. C. Scheibler and H. Mittelmeier, Ber. 1890, **23**, 3060, 3295, 3473; 1891, **24**, 301; 1893, **26**, 2930; abst. J. C. S. 1891, **60**, 33, 165, 284; J. S. C. I. 1890, **19**, 1140; 1891, **20**, 378. A. Herzfeld, Bied. Centr. 1880, **9**, 347; 1881, **10**, 203; abst. J. C. S. 1880, **50**, 866; 1881, **52**, 1024. Ber. 1879, **12**, 2120; 1885, **18**, 3469; abst. J. C. S. 1880, **50**, 310. J. Ducreux, E. P. 11896, 1904. F. P. 425714, 1911; abst. J. S. C. I. 1911, **30**, 974. Addn. dated Jan. 30, 1912 to F. P. 425714, 1911; abst. J. S. C. I. 1912, **31**, 742. A. Dobroslavine, J. Russ. Phys. Chem. Soc. 1876, **8**, I, 57; abst. Bull. Soc. Chim. 1875, **26**, 452; J. C. S. 1877, **32**, i, 453. A. Boidin, E. P. 16589, 1905; abst. J. S. C. I. 1906, **25**, 861; E. P. 8447, 1909; abst. J. S. C. I. 1909, **28**, 1265. Swiss P. 53952, 1910. Compt. rend. 1906, **143**, 511; abst. J. C. S. 1906, **90**, i, 933; Chem. News, 1906, **94**, 232; Chem. Centr. 1906, **75**, II, 1563; Jahr. Chem. 1905–1908, II, 4786; Wag. Jahr. 1905, **52**, II, 225. H. Sherman, School of Mines Quart. 1896, **17**, 356; abst. J. S. C. I. 1896, **15**, 832. H. Sherman and J. Baker, J. A. C. S. 1916, **38**, 1885; abst. J. S. C. I. 1916, **35**, 1076; J. C. S. 1916, **109**, i, 767. H. Sherman and J. Walker, J. A. C. S. 1917, **39**, 1476; abst. J. S. C. I. 1917, **36**, 974. H. Sherman and P. Punnett, J. A. C. S. 1916, **38**, 1877; abst. J. S. C. I. 1916, **35**, 1075. H. Sherman and M. Schlesinger, J. A. C. S. 1913, **35**, 1784; abst. J. C. S. 1913, **104**, i, 1400.

presence of phenol,[1] and other aromatic hydroxy compounds.

Takadiastase developed by J. Takamine,[2] and investigated by A. Hill[3] has been used in the determination of starch, as in the methods of C. Revis and H. Burnett,[4] and W. Davis and A. Daisch.[5] F. Ando[6] proposes to saccharify starch by koji-diastase.

Action of Acids on Starch. According to the earlier work of M. Berthelot,[7] C. Brunner,[8] Couverchel,[9] J. Daniell,[10] J. Doebereiner,[11] J. Emmet,[12] J. Fritzsche,[13] J. Gottlieb,[14] Mayet,[15] L. Melsens,[16] E. Monier,[17] F. Musculus,[18] Oswald,[19] A. Payen,[20] J. Per-

---

[1] W. Detmer, Bied. Centr. 1883, **12**, 71; abst. J. C. S. 1883, **44**, 631; Chem. News, 1884, **50**, 35; Zts. physiol. Chem. **7**, 1; Ber. 1882, **15**, 2924; Chem. Centr. 1882, **53**, 46; Jahr. Chem. 1882, **35**, 1233. Ber. Bot. 1893, 149.

[2] U. S. P. 975656, 1910. U. S. P. 991560, 1910; abst. J. S. C. I. 1910, **29**, 1468; C. A. 1911, **5**, 801, 2299, 2576.

[3] Compt. rend. 1901, **133**, 244; abst. Jahr. Chem. 1901, **54**, 1782; Chem. News, 1901, **84**, 23.

[4] Analyst, 1915, **40**, 429; abst. J. S. C. I. 1915, **34**, 1109; J. C. S. 1915, **108**, ii, 845; C. A. 1916, **10**, 226.

[5] J. Agric. Sci. 1914, **6**, 152; abst. J. C. S. 1914, **106**, ii, 588; J. S. C. I. 1914, **33**, 657. Zts. ang. Chem. 1914, **27**, I, 116; abst. Wag. Jahr. 1914, **60**, II, 249; C. A. 1914, **8**, 722, 2836.

[6] Eighth Inter. Cong. Appl. Chem. 1912, Sect. VI-B, Orig. Comm. **14**, 13; abst. J. S. C. I. 1912, **31**, 946; J. C. S. 1913, **104**, i, 919; C. A. 1913, **6**, 3097.

[7] Mem. Soc. Biol. 1857, **4**, 77; Brown-Sequard, J. de Physiol. 1859, **2**, 577; J. prakt. Chem. 1859, **76**, 371; J. de Pharm. 1858, **34**, 293; Nuovo Cimento, 1859, **10**, 383; Compt. rend. 1858, **47**, 227. Mem. Soc. Biol. 1857, **4**, 112; Ann. 1858, **106**, 117.

[8] Pogg. Ann. 1835, **34**, 319; abst. Berz. Jahr. Chem. 1837, **16**, 211, 213; Ann. 1835, **14**, 303.

[9] J. Pharm. 1821, **7**, 267; Ann. Chim. Phys. 1831, **46**, 147; Erdmann's J. Tech. Chem. 1831, **11**, 215; Flora, 1834, **17**, 273, 289; Mem. Savans Etrang. 1832, **3**, 206; Pogg. Ann. Phys. 1831, **32**, 398.

[10] Ann. Chim. Phys. 1819, **10**, 219; Quart. J. Sci. 1819, **6**, 32; N. J. Pharm. 1820, **4**, 182.

[11] Schw. J. 1812, **5**, 281.

[12] (Sill.) Amer. J. Sci. 1837, **32**, 140; J. prakt. Chem. 1837, **12**, 120; Berz. Jahr. Chem. 1837, **19**, 275; Bibl. Univ. 1837, **11**, 172.

[13] N. Ann. Sci. Nat. Bot. **10**, 161. Pogg. Ann. 1834, **32**, 129; Ann. 1834, **12**, 287. Oken, Isis, 1836, Col. 731.

[14] Ann. 1844, **52**, 121; abst. Berz. Jahr. 1846, **25**, 551.

[15] N. J. Pharm. 1847, **11**, 81; J. prakt. Chem. 1847, **40**, 435; abst. Jahr. Chem. 1847–1848, **1**, 794; Chem. Centr. 1847, **18**, 393.

[16] Inst. 1857, 160, 161; Acad. Sci. Bull. 1856, **23**, II, 663; abst. Jahr. Chem. 1857, **10**, 493.

[17] Compt. rend. 1858, **46**, 425; J. prakt. Chem. 1858, **73**, 479; abst. Jahr. Chem. 1858, **11**, 632; Dingl. Poly. 1858, **147**, 452; Chem. Gaz. 1858, 140; Poly. Centr. 1858, **24**, 624; Wag. Jahr. 1858, **4**, 415.

[18] J. pharm. chim. 1860, **37**, 419; Chem. Centr. 1860, **31**, 602; abst. Chem. News, 1860, **1**, 287; Compt. rend. 1860, **50**, 785; abst. Mon. Sci. 1859–1860, **2**, 710; Rep. Chim. appl. 1860, **2**, 140; Instit. 1860, 147; Dingl. Poly. 1860, **158**, 424; Jahr. Chem. 1860, **13**, 502; Wag. Jahr. 1860, **6**, 335.

[19] N. Br. Archiv. d. Pharm. 1844, **40**, 166; abst. Berz. Jahr. 1846, **25**, 550.

soz,[1] E. Scharling,[2] C. Schmidt,[3] P. Schuetzenberger[4] and K. Ventske,[5] it had been shown that by heating starch with dilute acids, the simplest expression of the starch molecule combines with one molecule of water to form glucose:

$$C_6H_{10}O_5 + H_2O = C_6H_{12}O_6$$

Moderately concentrated hydrochloric acid at room temperature, converts starch after a few days into a water-soluble modification without materially changing its microscopic appearance.[6] This material is apparently identical with the soluble starch prepared by the action of malt extract upon starch paste.[7] Continued action of 12% HCl in the cold produces amylodextrin.[8] Boiling dilute acids first convert starch into soluble starch, then into dextrin and maltose, intermediate products of undetermined constitution (amyloins) being also formed.[9] The higher the temperature and the longer the period of reaction, causes a complete conversion to take place.[10] This effect is best brought about by the employment of dilute acid.[11] Dilute nitric,[12] formic,[13] oxalic,[14]

---

20. Compt. rend. 1846, **23**, 487; 1847, **24**, 87; 1859, **48**, 775; abst. Jahr. Chem. 1859, **12**, 530, 539, 545, 563. J. pharm. chim. 1846, **10**, 460; 1859, **35**, 106. Rep. Chim. Pure, 1858–1859, **1**, 233.

[1] Compt. rend. 1843, **17**, 1067.

[2] Ann. 1842, **42**, 272.

[3] Ann. 1844, **51**, 31. N. Br. Arch. Pharm. **19**, 195; abst. Berz. Jahr. Chem. 1846, **25**, 564; Annuaire de Chimie, 1845, **1**, 318.

[4] Compt. rend. 1865, **61**, 485; abst. Bull. Soc. Chim. 1866, **5**, 291; Zts. Chem. 1866, **9**, 16; Chem. Centr. 1865, **36**, 1036; J. prakt. Chem. 1866, **97**, 250; J. pharm. chim. 1865, **2**, 376; Jahr. Chem. 1865, **18**, 594; Ber. 1869, **2**, 163, 556.

[5] J. prakt. Chem. 1842, **25**, 65; 1843, **28**, 101.

[6] E. Preuss, Zts. Spiritusind. 1904, **27**, 478; abst. J. S. C. I. 1904, **23**, 1228; Wag. Jahr. 1904, **50**, II, 226.

[7] C. Lintner, J. prakt. Chem. 1886, **142**, 378; abst. Chem. News, 1886, **54**, 298; J. C. S. 1887, **52**, 165; Bull. Soc. Chim. 1888, **49**, 834; Ber. 1886, **19**, R, 842; Jahr. Chem. 1886, **39**, 1886. H. Brown and G. Morris, J. C. S. 1889, **55**, 450; Chem. News, 1889, **59**, 295; Ber. 1889, **22**, R, 740; Chem. Centr. 1889, **60**, II, 124, 285; Jahr. Chem. 1889, **42**, 136, 2063; J. S. C. I. 1889, **8**, 716.

[8] Naegeli, "Beiträge z. Kenntniss d. Stärkegruppe."

[9] H. Brown, G. Morris and E. Moritz, E. P. 1809, 1889; abst. J. S. C. I. 1891, **10**, 265.

[10] F. Allihn, J. prakt. Chem. 1880, **130**, 46; abst. Dingl. Poly. 1883, **250**, 534; J. C. S. 1881, **40**, 149, 770; 1884, **46**, 721; J. S. C. I. 1884, **3**, 323; Bull. Soc. Chim. 1881, **35**, 224, 442; Ber. 1880, **13**, 1761; 1883, **16**, 2920; Jahr. Chem. 1883, **36**, 1622, 1745.

[11] L. Thorne and E. Jeffers, Seventh Inter. Cong. Appl. Chem. 1909; abst. J. S. C. I. 1909, **28**, 731; C. A. 1910, **4**, 1697; Zts. ang. Chem. 1909, **22**, 1274.

[12] Dextrin-Automat Ges., D. R. P. 286362, 1912; abst. J. S. C. I.

lactic,[1] and phosphoric acids[2] produce the same result. The results of W. de Coninck,[3] A. Roessing,[4] A. Daisch,[5] and S. Harvey[6] give experimental details. Hydrofluoric[7] and hydriodic acids,[8] have been used for this purpose to a limited extent only.

E. Parow[9] has studied the rapidity of conversion of potato starch by dilute sulfuric acid, as measured by the relative proportions of dextrose and dextrin in the extract under varying

---

1916, **35**, 63; Chem. Zentr. 1915, **86**, II, 515; Chem. Ztg. Rep. 1915, **39**, 326; Zts. ang. Chem. 1915, **28**, 476. W. Oeschner de Coninck and A. Raynaud, Rev. gen. Chim. Pure, Appl. 1910, **14**, 169; abst. J. C. S. 1912, **102**, i, 73. A. Doroschewsky and A. Rakowsky, J. Russ. Phys. Chem. Soc. 1907, **39**, 427; Chem. Zentr. 1907, **78**, II, 1325; J. C. S. 1907, **92**, i, 678; J. S. C. I. 1907, **26**, 1154. A. Doroschewsky, A. Rakowsky and A. Bardt, J. Russ. Phys. Chem. Soc. 1908, **40**, 932; abst. J. C. S. 1908, **94**, i, 767. A. Seyberlich and A. Trampedach, J. C. S. 1887, **52**, 792; abst. Chem. Centr. 1887, **58**, 346. U. S. P. 337448. E. P. 8000, 1885. F. P. 165905, 1885. D. R. P. 37236, 39573; abst. J. S. C. I. 1886, **5**, 453; 1887, **6**, 46; Chem. Tech. Rep. 1886, **25**, I, 112; 1887, **26**, II, 195; 1888, **27**, II, 171; Wag. Jahr. 1887, **33**, 874.

[13] J. Frankhauser, Ann. Agronom, **12**, 340; Der Bund (Berne), **37**, 126; abst. J. C. S. 1886, **50**, 1061.

[14] O. v. Friederichs, Arkiv. för Kemi. Min. och Geol. 1913, **5**, No. 2, 3; abst. Chem. Zentr. 1914, **85**, I, 660, 762; J. S. C. I. 1914, **33**, 327, 328.

[1] W. de Coninck and A. Raynaud, Bull. Acad. Roy. Belg. 1911, 438; abst. J. C. S. 1911, **100**, i, 770, 771; C. A. 1911, **5**, 2443, 2753, 3353, 3636; Chem. Zentr. 1911, **82**, I, 1816; II, 272, 273, 855.

[2] H. Endemann, Bied. Centr. 1884, 568; abst. J. C. S. 1885, **48**, 104. E. P. 6176, 1882. D. R. P. 24041; abst. Industbl. 1884, 47; J. S. C. I. 1883, **2**, 388; 1884, **3**, 114; Ber. 1884, **17**, R, 61; Chem. Ind. 1883, **6**, 338; Chem. Tech. Rep. 1883, **22**, II, 144; Wag. Jahr. 1883, **29**, 672.

[3] Bull. Acad. Roy. Belg. 1910, 515, 586, 848; abst. J. C. S. 1910, **98**, i, 655; 1911, **100**, i, 181. W. de Coninck and A. Raynaud, Bull. Acad. Roy. Belg. 1911, 213, 235; abst. J. C. S. 1911, **109**, i, 423; Bull. Soc. Chim. 1911, **9**, 586; abst. J. C. S. 1911, **100**, i, 607. H. Wilmot, E. P. 18358, 1894; abst. J. S. C. I. 1895, **24**, 879; Chem. Centr. 1896, **67**, I, 231.

[4] Zts. Offentl. Chem. 1903, **9**, 133; 1904, **10**, 61, 277; abst. Chem. Centr. 1903, **34**, I, 1378; 1904, **35**, I, 1177, II, 855; J. S. C. I. 1903, **22**, 886; 1904, **23**, 563, 953; J. S. C. I. 1904, **86**, ii, 298. Chem. Ztg. 1905, **29**, 867; abst. J. S. C. I. 1905, **24**, 979; J. C. S. 1905, **88**, i, 684.

[5] J. C. S. 1914, **105**, 2053, 2065; abst. J. S. C. I. 1914, **33**, 934; C. A. 1915, **9**, 196; Bull. Soc. Chim. 1915, **18**, 138, 139; Zts. ang. Chem. 1915, **28**, II, 340.

[6] Analyst, **11**, 221; abst. J. C. S. 1887, **26**, 125; Ber. 1887, **20**, R, 76.

[7] F. Malinsky, Zts. Spiritusind. 1899, **22**, 240; abst. J. S. C. I. 1899, **18**, 1037. D. R. P. 103592; abst. Chem. Centr. 1899, **70**, II, 892; Chem. Ztg. 1899, **23**, 724; Jahr. Chem. 1899, **52**, 404; Wag. Jahr. 1899, **45**, 725.

[8] W. de Coninck and A. Raynaud, Bull. Soc. Chim. 1911, **9**, 586; abst. J. S. C. I. 1911, **30**, 914; C. A. 1911, **5**, 2443, 2753, 3353, 3636; Chem. Zentr.1911, **82**, I, 1816; II, 272, 273, 855; J. C. S. 1911, **100**, i, 770, 771.

[9] E. Parow, Zts. Spiritusind. 1905, **28**, 121; 1906, **29**, 51; abst. J. S. C. I. 1905, **24**, 450; 1906, **25**, 225; Bied. Centr. 1905, **34**, 546; J. C. S. 1905, **88**, i, 684. E. Parow, Ellrodt and F. Neumann, Zts. Spiritusind, 1907, **30**, 430; abst. J. S. C. I. 1907, **26**, 1103. E. Parow and F. Neumann, Zts. Spiritusind. 1907, **30**, 561; abst. J. C. S. 1908, **94**, ii, 543; Chem. Zentr. 1908, **79**, I, 557.

conditions and tabulated his results. B. Tollens[1] found in the products of hydrolysis of potato starch with 8% sulfuric acid, dextrose, at best only traces of mannose and no galactose.[2]

As a summary of the work of A. Berge,[3] C. O'Sullivan,[4] F. Musculus and D. Gruber,[5] L. Bondonneau,[6] F. Salomon,[7] R. Sachsse,[8] L. Schulze,[9] L. Sostegni,[10] A. Seyberlich and A. Trampe-

[1] Ber. 1873, **6,** 1390; abst. J. C. S. 1874, **27,** 245, 565; Chem. Centr. 1873, **44,** 648. Ber. 1883, **16,** 921. Ber. 1906, **39,** 2190; abst. J. C. S. 1906, **90,** i, 560. Zts. ver. Deut. Zuckerind, 1906, 664; abst. J. S. C. I. 1906, **25,** 771. G. Topf, Zts. anal. Chem. 1887, **26,** 137.

[2] H. v. Vogel, Schw. J. 1812, **5,** 80; Ann. Chim. Phys. 1812, **82,** 148; Gilb. Ann. 1812, **42,** 123; Nicholson J. 1812, **33,** 274. A. Vogel, Ber. 1871, **4,** 140; abst. J. C. S. 1871, **24,** 226; Chem. News, 1871, **23,** 179; Jahr. Chem. 1871, **24,** 201.

[3] D. R. P. 47572, 1888; abst. Ber. 1889, **22,** 616; Wag. Jahr. 1889, **35,** 874; Chem. Tech. Rep. 1889, **28,** II, 59; Dingl. Poly. 1889, **274,** 563; Jahr. Chem. 1889, **42,** 2759. Belg. P. Feb. 4, 1890. E. P. 9320, 1888; 7272, 1891; abst. J. S. C. I. 1889, **8,** 633; 1892, **11,** 448. Bull. Assoc. Belg. Chimistes, **10,** 444; abst. J. S. C. I. 1897, **16,** 548. See also Soc. Anon. La Saccharification, F. P. 207361; abst. Rev. chim. ind. 1891, **2,** 20; Mon. Sci. 1891, **37,** 448. C. Pope, U. S. P. 570183, 585285.

[4] J. C. S. 1872, **25,** 579, 581; 1876, **30,** 478; **31,** 125; 1879, **35,** 772; abst. Chem. News, 1872, **25,** 250; 1876, **33,** 218; 1879, **40,** 238, 288; Bull. Soc. Chim. 1877, **27,** 81; 1879, **32,** 493; Mon. Sci. 1876, **18,** 1218; Ber. 1872, **5,** 485; 1876, **9,** 650, 949; Chem. Centr. 1876, **47,** 564; Chem. Tech. Rep. 1872, **11,** II, 46; Jahr. Chem. 1872, **25,** 771; 1876, **29,** 837, 838, 1147; 1879, **32,** 845; Wag. Jahr. 1876, **22,** 717; Bayer. Bierbrauer, 1876, 91. Rep. Anal. Chem. 1884, **11,** Chem. News, 1883, **48,** 244. J. C. S. 1884, **43,** 1; abst. Ber. 1884, **17,** R, 88; Chem. Tech. Rep. 1884, **23,** I, 249; Jahr. Chem. 1884, **37,** 1635. C. O'Sullivan, Proc. Chem. Soc. 1904, **20,** 65; J. C. S. 1904, **85,** 616; abst. J. S. C. I. 1904, **23,** 449; Jahr. Chem. 1904, **57,** 1153; Bull. Soc. Chim. 1904, **32,** 1175.

[5] Compt. rend. 1878, **86,** 1459; abst. Chem. News, 1878, **38,** 33, 115; J. C. S. 1878, **34,** 778; Bull. Soc. Chim. 1878, **30,** 54; J. pharm. chim. 1878, **28,** 308; Ber. 1879, **12,** 287; Chem. Tech. Rep. 1878, **17,** II, 137; Jahr. Chem. 1878, **31,** 924.

[6] Compt. rend. 1875, **81,** 972, 1212; abst. Chem. News, 1875, **32,** 281; **33,** 18; J. C. S. 1876, **29,** 365; Bull. Soc. Chim. 1876, **25,** 2; J. pharm. chim. 1876, **23,** 34; Ber. 1876, **9,** 61, 69; Jahr. Chem. 1875, **78,** 789.

[7] Ber. 1882, **15,** 3100; 1883, **16,** 2509; J. prakt. Chem. 1882, **133,** 348; **134,** 324; 1883, **136,** 82, 122; abst. J. C. S. 1884, **46,** 36; J. S. C. I. 1882, **1,** 329; Bull. Soc. Chim. 1884, **42,** 292; J. pharm chim. 1885, **11,** 535; Jahr. Chem. 1882, **35,** 1124; 1883, **36,** 1366; 1884, **37,** 1408; 1885, **38,** 1756.

[8] Chem. Centr. 1877, **48,** 732; Leipziger Naturforsch. Gess. Ber. 1877, 30; abst. Chem. News, 1879, **39,** 264; Chem. Tech. Rep. 1878, **17,** I, 297; Jahr. Chem. 1877, **30,** 898; Jahr. rein Chem. 1877, **5,** 175; Zts. Chem. Grossgewerbe, 1877, **2,** 588.

[9] J. prakt. chem. 1883, **136,** 311; abst. Chem. News, 1884, **49,** 70; J. C. S. 1884, **46,** 284; Bull. Soc. Chim. 1884, **42,** 292; Ber. 1883, **16,** 1364; Chem. Tech. Rep. 1883, **22,** II, 133; Chem. Ztg. 1883, **7,** 1552; Jahr. Chem. 1883, **36,** 1366; Wag. Jahr. 1883, **29,** 671; Zts. deut. Spiritusfabr. 1883, 1022.

[10] Gaz. chim. ital. 1885, **15,** 376; abst. J. C. S. 1886, **50,** 221; 1888, **54,** 126; J. pharm. chim. 1886, **13,** 130; Ber. 1885, **19,** 103; Jahr. Chem. 1885, **38,** 1756.

dach,[1] Naegeli,[2] H. Johnson,[3] G. Rolfe, G. Defren, W. Faxon and H. Geromanos,[4] C. Sovereign and A. Lenders,[5] W. Squire,[6] G. Defren,[7] C. Duryea[8] and A. Fernbach and M. Schoen,[9] it may be stated that dextrose is the final hydrolytic product, but that the action of acids continues on the dextrose, yielding compounds as yet imperfectly investigated. The immediate substances dextrin and maltose are first produced, the rapidity of the change being dependent upon the strength of the acid, the temperature and the pressure. The maximum production of dextrose takes place when pressure and 1.5%–2.0% of acid is used, and the proportion of dry starch to acid solution does not exceed 1 to 3.

The colloidal body, gallisin, found in commercial glucose,[10] is identical with the isomaltose of E. Fischer[11] obtained by the

[1] U. S. P. 337448. E. P. 8000, 1885. F. P. 165905, 1885. D. R. P. 37236, 39573; abst. J. C. S. 1887, **52**, 792; J. S. C. I. 1886, **5**, 453; 1887, **6**, 46; Ber. 1886, **19**, R, 863; 1887, **20**, R, 409; Chem. Centr. 1887, **58**, 376; Chem. Tech. Rep. 1886, **25**, I, 112; 1887, **26**, II, 195; 1888, **27**, II, 171; Jahr. Chem. 1886, **39**, 2129; 1887, **40**, 2632, 2661; Tech. Chem. Jahr. 1885-1886, **8**, 295; Wag. Jahr. 1887, **33**, 874; Zts. Chem. Ind. 1887, **1**, 348. N. Zts. Rübenzuckerind. 1885, **17**, 186; Industbl. 1886, 70; Zts. Spiritusind. 1885, 107; La Sucrerie indigene et coloniale, 1885, **26**, 507; Chem. Ztg. Rep. 1888, **12**, 51; Zts. Ver. Rübenzuckerind. im Zollverein, 1888, 84.

[2] Stärkegruppe, Leipzig, 1874, 33, 99.

[3] Proc. Chem. Soc. 1898, 106; abst. J. S. C. I. 1898, **17**, 477; J. C. S. 1898, **73**, 490; Bull. Soc. Chim. 1899, **22**, 184; Chem. Centr. 1898, **69**, I, 1292; II, 279; Jahr. Chem. 1898, **51**, 1352.

[4] J. A. C. S. 1896, **18**, 869; 1897, **19**, 6981; 903, **25**, 1003, 1015; abst. J. S. C. I. 1897, **16**, 167, 1048; 1903, **22**, 1252; J. C. S. 1904, **86**, i, 17; Ber. 1896, **29**, R, 1156; Chem. Centr. 1897, **68**, II, 918; 1903, **74**, II, 1318; Jahr. Chem. 1897, **50**, 1514; 1903, **56**, 995, 1006.

[5] U. S. P. 948485, 1910; 1183408, 1916; abst. J. S. C. I. 1910, **29**, 367; 1916, **35**, 750; C. A. 1910, **4**, 1113; 1916, **10**, 1943; Chem. Ztg. Rep. 1910, **34**, 127. See also Soc. Franc. des Distilleries de l'Indo-Chine. F. P. 449155, 1911; 459634, 459815, 1912; abst. J. S. C. I. 1913, **32**, 502, 1166; Mon. Sci. 1914, **81**, 42; C. A. 1914, **8**, 3215; Chem. Ztg. Rep. 1914, **38**, 392, 393.

[6] J. S. C. I. 1884, **3**, 543; abst. Chem. Ind. 1884, **7**, 290; Jahr. Chem. 1884, **37**, 1802.

[7] Orign. Comm. Eighth Inter. Cong. Appl. Chem. 1912, **13**, 111; abst. J. S. C. I. 1912, **31**, 892; J. C. S. 1913, **104**, i, 832, C. A. 1912, **6**, 3034, 3155.

[8] Abst. J. S. C. I. 1911, **30**, 789; J. C. S. 1911, **100**, i, 711; C. A. 1911, **5**, 3353; Rep. Chim. 1911, **11**, 461; Chem. Zentr. 1911, **82**, II, 749.

[9] Bull. Soc. Chim. 1912, **11**, 303; abst. J. S. C. I. 1912, **31**, 402; C. A. 1912, **6**, 1552; Chem. Zentr. 1912, **83**, I, 1617; Meyer Jahr. Chem. 1912, **22**, 430.

[10] C. Schmitt and A. Cobenzl, Ber. 1884, **17**, 1000; abst. J. C. S. 1884, **46**, 981; J. S. C. I. 1884, **3**, 453; Bull. Soc. Chim. 1885, **44**, 155; Jahr. Chem. 1884, **37**, 1406. C. Schmitt and J. Rosenhek, Ber. 1884, **17**, 2456; abst. J. C. S. 1885, **48**, 134; Bull. Soc. Chim. 1886, **45**, 24; Jahr. Chem. 1884, **37**, 1406.

[11] Ber. 1890, **23**, 3687; abst. J. C. S. 1891, **60**, 412; J. S. C. I. 1891, **10**, 377; Chem. Centr. 1891, **62**, I, 539; Jahr. Chem. 1890, **43**, 2141.

action of concentrated HCl on dextrose.[1] Starch may also be inverted by platinum black.[2]

Further details on the action of acids upon starch is to be found in the work of Societe d'Exploitation des Processes H. Boulard,[3] C. Rheinfels,[4] S. Lillie,[5] F. Jewson,[6] F. Grueters,[7] H. Gayon and E. Dubourg,[8] G. Flourens,[9] L. Aubert and V. Giraud,[10] E. Donath,[11] W. Hiepe,[12] F. Roehmann,[13] Roehr,[14] H. Ost,[15] M. Stumpf,[16] J. Ducreux,[17] H. Wulkan and H. Straetz[18] and Societe des

---

[1] C. Scheibler and H. Mittelmeier, Ber. 1891, **24**, 301; abst. J. C. S. 1891, **60**, 536; J. S. C. I. 1891, **10**, 378; Bull. Soc. Chim. 1891, **6**, 678; Chem. Centr. 1891, **62**, I, 532; Jahr. Chem. 1891, **44**, 2175.

[2] C. Neilson, Am. J. Physiol. 1906, **15**, 412; J. C. S. 1906, **90**, i, 235; Chem. Centr, 1906, **75**, I, 1152; Jahr. Chem. 1905–1908, II, 943.

[3] F. P. 464601, 1913; 475792, 477927, 1914; abst. J. S. C. I. 1916, **35**, 11, 64, 1170; C. A. 1915, **9**, 1223; 1916, **10**, 1716. E. P. 25406, 1913.

[4] Woch. f. Brau. 1906, **23**, 510; abst. J. S. C. I. 1906, **25**, 998.

[5] U. S. P. 959237, Re. 13592, 1910; 1038397, 1023257, 1014311, 1014237, 1912; abst. J. S. C. I. 1910, **29**, 834; 1912, **31**, 197, 505, 945; Chem. Ztg. Rep. 1910, **34**, 303; 1912, **36**, 296, 483; C. A. 1912, **6**, 693, 1690, 3539; Mon. Sci. 1193, **79**, 111.

[6] E. P. 12291, 1906; abst. J. S. C. I. 1907, **26**, 704.

[7] Zts. ang. Chem. 1904, **17**, 1169; abst. J. S. C. I. 1904, **23**, 875; J. C. S. 1904, **86**, i, 852; Chem. Centr. 1904, **75**, II, 825; Jahr. Chem. 1904, **57**, 1153; Tech. Chem. Jahr. 1904, **27**, 262; Wag. Jahr. 1904, **50**, II, 224.

[8] Compt. rend. 1886, **103**, 885; abst. J. S. C. I. 1887, **6**, 144; abst. J. C. S. 1887, **52**, 171; Chem. News, 1886, **54**, 273; Bull. Soc. Chim. 1887, **47**, 649; Ber. 1887, **20**, R, 13; Chem. Tech. Rep. 1887, **26**, II, 95; Jahr. Chem. 1888, **41**, 2499.

[9] Compt. rend. 1890, **110**, 1204; abst. J. C. S. 1890, **58**, 1089; J. S. C. I. 1890, **19**, 815; Bull. Soc. Chim. 1891, **5**, 716; Ber. 1890, **23**, 461; Jahr. Chem. 1890, **43**, 2152.

[10] D. R. P. 32388, 1884; abst. J. C. S. 1885, **48**, 1274; Ber. 1885, **18**, 674; Chem. Ind. 1885, **8**, 292; Chem. Tech. Rep. 1885, **24**, II, 143; Jahr. Chem. 1885, **38**, 2146; Tech. Chem. Jahr. 1885–1886, **8**, 291; Wag. Jahr. 1885, **31**, 764. Dingl. Poly. 1885, **257**, 298.

[11] Chem. Ztg. 1891, **15**, 597; abst. J. S. C. I. 1891, **10**, 843; Jahr. Chem. 1891, **44**, 2735. J. prakt. Chem. 1894, **49**, 546; abst. J. C. S. 1894, **66**, i, 436; J. S. C. I. 1894, **13**, 823; Bull. Soc. Chim. 1894, **12**, 1463; Ber. 1894, **27**, R, 574; Jahr. Chem. 1894, **49**, 546.

[12] The Country Brewers Gaz. 1893, No. 431; 1894, No. 433, 434, 435; abst. J. S. C. I. 1894, **13**, 264; Woch. f. Brau. **11**, 28; Chem. Centr. 1894, **65**, I, 417; Jahr. Chem. 1894, **47**, 1116.

[13] Biochem. Zts. 1917, **84**, 399; abst. J. C. S. 1918, **114**, i, 138; C. A. 1918, **12**, 1300; J. S. C. I. 1918, **37**, 162-A.

[14] Bied. Centr. 1880, **9**, 547; abst. J. C. S. 1880, **38**, 932; Chem. Tech. Rep. 1880, **19**, I, 108.

[15] Chem. Ztg. 1895, **19**, 1501; abst. J. S. C. I. 1895, **14**, 877, 895. Ber. 1913, **46**, 2995; abst. J. C. S. 1913, **104**, i, 1148. H. Ost, F. Westhoff and L. Gessner, Ann. 1911, **382**, 340; abst. J. S. C. I. 1911, **30**, 1024.

[16] Oest. Ver. Zuckerind. 1878, 25. Zts. Spiritusind. 1878, 259. Bied. Centr. 1880, **9**, 457; abst. J. C. S. 1880, **38**, 834.

[17] Addn. dated Jan. 30, 1912 to F. P. 425714, 1911; abst. J. S. C. I 1911, **30**, 974; 1912, **31**, 742.

[18] E. P. 13659, 1900; abst. J. S. C. I. 1901, **20**, 824. Aust. P. 5792,

Produits Amylaces,[1] as well as numerous other investigators.

F. Soxhlet first showed in 1881 that starch subjected to the action of water under high pressure was converted into sugar when a temperature of 149° was reached.[2]

The action of concentrated nitric and sulfuric acids upon starch results in the formation of starch nitrates, explosive esters which are described in detail in a succeeding chapter of this volume.

Amylose, or amylocellulose, separates when starch solution or starch paste is allowed to stand for some time. It is partially soluble in boiling water and completely so in water at 150°. The solutions are devoid of gelatinizing power, but give with iodine a blue coloration, and are quantitatively converted by diastase into maltose. Amyloid exists in a liquid form by heating under pressure to 150°, and upon cooling the solution the material separates out in a granular form.

T. Chrzaszcz and K. Terlikowski[3] have studied the power

1901. H. Wulkan, U. S. P. 696156, 1912; abst. J. S. C. I. 1902, **21**, 630. D. R. P. 223301, 1908; abst. J. S. C. I. 1910, **29**, 1264. H. Wulkan and Dextrin Automat Ges. U. S. P. 1139620, 1915; abst. J. S. C. I. 1915, **34**, 727.

[1] E. P. 3930, 1902; abst. J. S. C. I. 1903, **22**, 152. Addn. dated March 11, 1902 to F. P. 316582, 1901; abst. J. S. C. I. 1902, **21**, 1545.

[2] F. Soxhlet, Bied. Centr. 1881, **10**, 554; abst. J. C. S. 1882, **42**, 30. Zts. f. ges. Br. 1881, 177. Zts. Spiritusind. 1884, 195. Zts. anal. Chem. 1885, **24**, 618. T. van Korvin Sakovicz, E. P. 718, 1883; abst. J. S. C. I. 1883, **2**, 483. Wahl-Henius Research Laboratory and R. Wahl, E. P. 101406, 1916; abst. J. S. C. I. 1917, **36**, 936.

[3] Woch. Brauw. 1912, **29**, 590, 607, 623, 636; abst. J. S. C. I. 1912, **31**, 1089. T. Chrzakzcz, Zts. Spiritusind. 1909, **32**, 520, 535, 539, 544, 556, 557, 569, 571, 578; 1911, **34**, 545; abst. C. A. 1912, **6**, 1050; J. C. S. 1910, **98**, ii, 994; 1912, **102**, i, 402; J. S. C. I. 1910, **29**, 103; 1911, **30**, 1401; Chem. Zentr. 1910, **81**, I, 288; Jahr. Chem. 1910, **63**, 1640; Meyer Jahr. Chem. 1909, **19**, 414, 426. T. Chrzakzcz and S. Pierozek, Zts. Spiritusind. 1910, **33**, 66, 81, 98, 132, 145; abst. C. A. 1910, **4**, 2540; 1911, **5**, 755; J. S. C. I. 1910, **29**, 583; Chem. Zentr. 1910, **81**, I, 1535; Wochenschr. f. Brauerei, **27**, 69, 89, 98, 120, 134, 151, 163, 175, 186, 199. See also H. Brown and J. Heron, J. C. S. 1879, **35**, 596; abst. Chem. News, 1879, **39**, 284; J. C. S. 1880, **41**, 22; **42**, 62; 1881, **43**, 154; Ann. 1879, **199**, 165; Ber. 1879, **12**, 1477; Chem. Tech. Rep. 1879, **8**, II, 163; Jahr. rein Chem. 1879, **7**, 507; Jahr. Chem. 1879, **32**, 838; Zts. Chem. Grossgewerbe, 1879, **6**, 153, 254, 259; Zts. ges. Brauw. **14**, 442. See A. Herzfeld, Ber. 1879, **12**, 2120; abst. Jahr. rein Chem. 1879, **7**, 508; Zts. ges. Brauw. **14**, 449; Zts. Chem. Grossgewerbe, 1879, **6**, 153. H. Brown and G. Morris, J. C. S. 1885, **47**, 527; abst. Chem. News, 1885, **51**, 308; J. S. C. I. 1885, **4**, 682; Bull. Soc. Chim. 1888, (2), **50**, 390; Ber. 1885, **18**, 615; Ann. 1885, **231**, 72; Jahr. Chem. 1885, **38**, 1757, 1758. H. Brown and G. Morris, Proc. Chem. Soc. 1895, (148), 35; J. C. S. 1895, **67**, 309, 709; abst. J. S. C. I. 1895, **14**, 288; Bull. Soc. Chim. 1897, (3), **18**, 871, 936, 937; Ber. 1895, **28**, 642; 1896, **29**, 1135; Chem. Tech. Rep. 1895, **34**, II, 112; Chem. Ztg. 1899, **13**, 1356. In this connection, see also Chem. News, 1886, **53**, 37; 1888, **57**,

of amylase to liquefy starch grains. In experiments made by A. Fernbach[1] on the action of small amounts of amylase on an excess of starch, it was found that the action was most rapid under conditions of neutrality to helianthin, in contradistinction to the results of L. Maquenne and E. Roux, who found an alkaline reaction most favorable.[2]

F. Botazzi and C. Victoroff[3] have been able to corroborate the work of Fouard[4] along the lines that the amylose of starch forms a colloidal solution with water which is perfectly clear and transparent, but is non-dialyzable, but can be filtered through

---

196; 1889, **59**, 295; 1895, **72**, 45. A. Hill, Proc. Chem. Soc. 1898, 156; J. C. S. 1898, **73**, 634; abst. Chem. News, 1897, **78**, 19; J. S. C. I. 1898, **17**, 684; Bull. Soc. Chim. 1899, (3), **22**, 669; Chem. Centr. 1898, **69**, II, 632; Jahr. Chem. 1898, **51**, 222; Meyer Jahr. Chem. 1898, **8**, 149, 257; Zts. physik. Chem. 1899, **29**, 171. Proc. Chem. Soc. 1901, **17**, 184; abst. Chem. News, 1901, **83**, 138; J. S. C. I. 1901, **20**, 491, 736; Rept. Chem. 1901, **1**, 544; Chem. Centr. 1901, **72**, I, 823; II, 437; Jahr. Chem. 1901, **54**, 876; Meyer Jahr. Chem. 1901, **11**, 349; Zts. ang. Chem. 1901, **14**, 344; Rev. phys. Chim. 1901, **5**, 517; Zts. ges. Brauw. **24**, 627. Ber. 1901, **34**, 600, 1380; abst. Chem. News, 1901, **84**, 23; J. C. S. 1901, **80**, 452; Jahr. Chem. 1901, **54**, 1780. J. Physiol. **28**, XXVI; abst. J. C. S. 1902, **82**, ii, 515. Proc. Chem. Soc. 1903, **19**, 99; J. C. S. 1903, **83**, 578; abst. Chem. News, 1903, **87**, 198; J. S. C. I. 1903, **22**, 505; Bull. Soc. Chim. 1903, (3), **30**, 298; Chem. Centr. 1903, **74**, I, 1115; II, 1334; Jahr. Chem. 1903, **56**, 240; Zts. physik. Chem. 1904, **48**, 249. A. Ling and B. Davis, J. Fed. Inst. Brewing, (4), **8**, 475; abst. Zts. Brauw. 1902, 556; J. C. S. 1902, **82**, i, 732; J. S. C. I. 1902, **21**, 1088; Chem. Centr. 1902, **73**, II, 1223; Jahr. Chem. 1902, **55**, 1991; Wag. Jahr. 1902, **48**, II, 414. C. Lintner and E. Kroeber, Ber. 1895, **28**, 984, 1034, 1050; abst. Zts. ges. Brauw. 1895, 153; J. C. S. 1895, **68**, i, 429; J. S. C. I. 1895, **14**, 690; Bull. Soc. Chim. 1896, (3), **16**, 647; Chem. Centr. 1895, **66**, II, 66, 163; Chem. Tech. Rep. 1895, **34**, I, 275; Chem. Ztg. Rep. 1895, **19**, 142; Jahr. Chem. 1895, **48**, 3012; Meyer Jahr. Chem. 1895, **5**, 189, 241; Wag. Jahr. 1895, **41**, 859, 861. J. Wolff and A. Fernbach, Compt. rend. 1903, **137**, 718; abst. J. S. C. I. 1903, **22**, 1302; Bull. Soc. Chim. 1904, (3), **31**, 766; Chem. Centr. 1903, **74**, II, 1451; Jahr. Chem. 1903, **56**, 1912.

[1] Compt. rend. 1906, **142**, 285; abst. J. C. S. 1906, **90**, i, 327; J. S. C. I. 1906, **25**, 192; Rep. Chim. 1906, **6**, 187; Chem. Ztg. Rep. 1906, **25**, 385; Chem. Zts. 1907, **6**, 40, 266; Jahr. Chem. 1905–1908, II, 4670; Wag. Jahr. 1906, **52**, II, 339, 350; Ann. de la Brass. 1906, No. 5, 12; Woch. f. Brauer. 1906, **23**, 159, 160; Zts. Bierbr. 1906, 349.

[2] Compt. rend. 1906, **142**, 124; abst. J. C. S. 1906, **90**, i, 327; J. S. C. I. 1906, **25**, 192; Rep. Chim. 1906, **6**, 174; Chem. Zts. 1907, **6**, 266; Jahr. Chem. 1905–1908, II, 4670; Wag. Jahr. 1906, **52**, II, 225.

[3] Atti. R. Accad. Lincei, 1910, (5), **19**, 7; abst. J. C. S. 1910, **98**, i, 655; C. A. 1911, **5**, 1406; J. S. C. I. 1910, **29**, 1323; Bull. Soc. Chim. 1911, (4), **10**, 883; Rep. Chim. 1911, **11**, 10; Chem. Zentr. 1910, **81**, II, 969; Jahr. Chem. 1910, **63**, II, 408; Woch. f. Brauer. 1910, **27**, 575.

[4] Compt. rend. 1908, **147**, 813; abst. J. C. S. 1908, **94**, i, 953; Bull. Soc. Chim. 1908, (4), **3**, 1170; Chem. Zentr. 1908, **79**, II, 2000; Jahr. Chem. 1905–1908, II, 940. See also Compt. rend. 1908, **147**, 931; 1909, **148**, 502; abst. J. S. C. I. 1908, **27**, 1215; Jahr. Chem. 1905–1908, II, 940; Wag. Jahr. 1909, **55**, II, 226; Chem. Ztg. 1908, **32**, 247, 520, 597, 771, 1178, 1215.

hardened gelatin under pressure (ultra filtration). When an electric current is passed through it, no migration. The amylopectin of starch forms with water a suspension in which the granules are ultramicroscopically visible.

The investigations of L. Maquenne[1] and L. Maquenne and E. Roux,[2] show that starch deposited in a granular form resembling natural starch grains from E. Fouard's starch solution[3] is identical with the amylose described by Maquenne.[4] Its resemblance to natural starch has led to the conclusion that starch consists of a perfect solution of amylose thickened by amylopectin. The opalescence and precipitation observed by Fouard in the phenomenon called "retrogradation" by Maquenne and Roux, who suggested that it is due to either pseudo-crystallization or to a polymerization similar to those undergone by certain sugars, dihydroxyacetone.

C. Tanret[5] found starches from many sources to contain

---

[1] Compt. rend. 1908, **146**, 317, 542; abst. C. A. 1908, **2**, 1522, 1631, 1647; J. C. S. 1908, **94**, i, 249; J. S. C. I. 1908, **27**, 291; Bull. Soc. Chim. 1908, (4), **3**, 403; Rep. Chim. 1908, **8**, 230; Chem. Zentr. 1908, **79**, I, 1264; II, 1534; Jahr. Chem. 1905–1908, II, 944; Wag. Jahr. 1908, **54**, II, 193.

[2] Compt. rend. 1906, **142**, 124; abst. J. C. S. 1906, **90**, i, 327; J. S. C. I. 1906, **25**, 192; Rep. Chim. 1906, **6**, 174; Chem. Zts. 1907, **6**, 266; Jahr. Chem. 1905–1908, II, 4670; Wag. Jahr. 1906, **52**, II, 225; Ann. Chim. Phys. 1906, (8), **9**, 179. L. Maquenne, Compt. rend. 1903, **137**, 88, 658, 797, 1266; abst. J. C. S. 1903, **84**, i, 679; 1904, **86**, i, 17, 18; Bull. Soc. Chim. 1903, (3), **29**, 1218; Rep. Chim. 1904, **4**, 57, 102, 130, 177; Chem. Centr. 1903, **74**, II, 757; 1904, **75**, I, 16, 361, 467; Chem. Zts. 1903–1904, **3**, 642; Jahr. Chem. 1903, **56**, 1005; Wag. Jahr. 1904, **50**, II, 224. Ann. Chim. Phys. 1904, (8), **2**, 124; abst. J. C. S. 1904, **86**, i, 800; Rep. Chim. 1904, **4**, 318; Chem. Centr. 1903, **74**, II, 557; 1904, **75**, I, 16, 1576; Jahr. Chem. 1904, **57**, 1151. Compt. rend. 1904, **138**, 213; abst. J. C. S. 1904, **86**, i, 294; J. S. C. I. 1904, **23**, 197; Rep. Chim. 1904, **4**, 202; Chem. Centr. 1904, **75**, I, 682; Jahr. Chem. 1904, **57**, 1151; Wag. Jahr. 1904, **50**, II, 224. Compt. rend. 1904, **138**, 375; abst. J. C. S. 1904, **86**, i, 294; J. S. C. I. 1904, **23**, 261; Rep. Chim. 1904, **4**, 250; Chem. Centr. 1904, **75**, I, 819; Jahr. Chem. 1904, **57**, 1151, 2150. See also Chem. News, 1903, **87**, 90; **88**, 269, 305; 1904, **89**, 59, 101.

[3] Compt. rend. 1908, **146**, 285, 978; abst. C. A. 1908, **2**, 197, 1380, 2330; J. C. S. 1908, **94**, i, 138, 503; J. S. C. I. 1908, **27**, 238, 635; Bull. Soc. Chim. 1908, (4), **3**, 836, 1170, 1182; Rep. Chim. 1908, **8**, 204, 404; Chem. Zentr. 1908, **7**, I, 1264; II, 1098; Jahr. Chem. 1905–1908, II, 937, 939; Wag. Jahr. 1908, **54**, II, 193. Bull. Assoc. Sucr. dist. **24**, 1207; **25**, 165; abst. C. A. 1907, **1**, 1781; 1908, **2**, 197; Compt. rend. 1907, **144**, 1368; Rep. Chim. 1908, **8**, 33. See also J. C. S. 1907, **92**, i, 391, 677; Bull. Soc. Chim. 1908, (4), **3**, 402, 757, 836, 1110; C. A. 1908, **2**, 1522, 1631, 1647.

[4] Compt. rend. 1905, **140**, 1303; abst. Chem. News, 1905, **91**, 279; J. C. S. 1905, **88**, i, 511; J. S. C. I. 1905, **24**, 630; Bull. Soc. Chim. 1905, (3), **33**, 723; Rep. Chim. 1905, **5**, 318; Chem. Centr. 1905, **76**, II, 121, 314; Chem. Zts. 1906, **5**, 10; Meyer Jahr. Chem. 1910, **15**, 410; Biochem. Centr. 1905–1906, **4**, 138, 380; Tech. Chem. Jahr. 1905, **28**, 274.

[5] Compt. rend. 1909, **146**, 1775; abst. C. A. 1909, **3**, 2676; J. C. S. 1909, **96**, i, 556; J. S. C. I. 1909, **28**, 847; Bull. Soc. Chim. 1909, (4), **5**, 310,

amylopectin and amylose, the amylopectin content ranging from 67% in chestnut starch to 79.5% in banana. The amylose from different starches appears to possess varying solubilities in water. Z. Gatin-Gruzewska[1] claims to have separated amylopectin and states that it forms the envelope of the starch granule, consisting of a plurality of sacs fitting one into the other, these being insoluble in cold water, but swelling in hot water to a gelatinous paste.

With alkali, amylopectin gives opalescent solutions which are dextro-rotatory. Amylose dried to a fine powder partially dissolves in cold water, and entirely so in hot water, and coloring iodine blue. It rapidly dissolves in the presence of minute amounts of alkali, and the alkaline solutions are dextro-rotatory.

Additional recent data on the nature of solutions of starch in formalin,[2] the modifying of starch,[3] preparation of stable solutions of starch and oxalic acid,[4] autolysis of starch,[5] sizing with starch,[6] starch adhesives,[7] diastatic properties of formaldehyde,[8] artificial ageing of starch,[9] substitutes[10], and the enzymatic hydrolysis of starch,[11] indicate the latest tendencies in research.

823; Rep. Chim. 1910, **10,** 66; Chem. Ztg. 1909, **33,** 837; Jahr. Chem. 1910, **62,** II, 374; Wag. Jahr. 1909, **55,** II, 226. Compt. rend. 1914, **158,** 1353; **159,** 530; abst. C. A. 1914, **8,** 2964; 1915, **9,** 1912, 2323; J. C. S. 1914, **106,** i, 665, 1167; J. S. C. I. 1914, **33,** 607, 1068; Bull. Soc. Chim. 1914, (4), **15,** 702; 1915, (4), **17,** 83.

[1] Compt. rend. 1908, **146,** 540; abst. C. A. 1908, **2,** 1631; J. C. S. 1908, **94,** i, 320; J. S. C. I. 1908, **27,** 415; Bull. Soc. Chim. 1908, (4), **3,** 1007; Rep. Chim. 1908, **8,** 276; Chem. Zentr. 1908, **79,** I, 1534; Jahr. Chem. 1905–1908, II, 931; Wag. Jahr. 1908, **54,** II, 193. See also Compt. rend. Soc. Biol. 1908, **64,** 178.

[2] M. Jacoby, Ber. 1919, **52,** B, 558; abst. C. A. 1919, **13,** 2528. W. v. Kaufmann and A. Lewite, Ber. 1919, **52,** B, 616; abst. C. A. 1919, **13,** 2528. See W. Kaufmann, Ber. 1917, **50,** 198; abst. J. C. S. 1917, **112,** i, 251; C. A. 1917, **11,** 2792. G. Woker, Ber. 1917, **50,** 679; abst. J. C. S. 1917, **112,** I, 447; C. A. 1917, **11,** 3259.

[3] R. Stutzke, U. S. P. 1320719, 1919; abst. J. S. C. I. 1920, **38,** 37-A.; C. A. 1920, **14,** 231.

[4] A. Junk, Chem. Ztg. 1919, **43,** 258; abst. C. A. 1920, **14,** 36.

[5] W. Biedermann, Fermentforschung, 1916, **1,** 474; 1919, **2,** 458; abst. Chem. Zentr. 1919, **90,** III, 635; J. S. C. I. 1917, **36,** 230; 1919, **38,** 958-A; J. C. S. 1917, **112,** i, 62.

[6] J. Whittaker, E. P. 130204, 1918; abst. C. A. 1920, **13,** 105.

[7] J. Paiton, U. S. P. 13181061919; abst. C. A. 1920, **14,** 105.

[8] H. Sallinger, Ber. 1919, **52,** B, 651; abst. C. A. 1919, **13,** 2529.

[9] Ibid., Kolloid. Zts. 1919, **25,** 111; abst. J. S. C. I. 1920, **39,** 76-A.

[10] A. Winter, Farber Ztg. 1919, **30,** 104; abst. C. A. 1919, **13,** 2605.

[11] H. Sherman and F. Walker, J. A. C. S. 1919, **41,** 1866; abst. J. S. C. I. 1920, **39,** 37-A. H. Sherman, F. Walker and M. Caldwell, J. A. C. S. 1919, **41,** 1123; abst. J. S. C. I. 1919, **13,** 651-A. G. Johnston, Austral. P. 5593, 1917.

CHAPTER III.

COTTON.

The official definition for cotton in the United States[1] is "the hairs of the seed from one or more of the cultivated varieties of *Gossypium herbaceum* Linne. (Fam. *Malvaceae*), freed from adhering impurities and linters and deprived of fatty matter." This refers to the mechanically purified filament. In Great Britain purified cotton is designated as[2] "the hairs of the seed of *Gossypium barbadense* Linne., and of other species of *Gossypium*, freed from fatty matter."

History of Cotton. As a textile cotton appears to have been used from the earliest times, the first reference to the use of cotton going back to 800 B.C.[3] Herodotus (Book 3), when writing of India, mentions "trees bearing a sort of wool instead of fruit, which was better and finer than that of sheep." He refers to the use of cotton clothes by the Indians. In 500 B.C., India employed cotton to a large extent for textile purposes, and early records show that hand spinning, weaving and dyeing were extensively developed. Spain seems to have been the first European country to produce cotton goods, the industry flourishing in that country from about the middle of the 13th century. Ages earlier, however, India, Egypt, and China had made use of the fiber.

In Pliny's History (19, 5), there is described a "kind of cloth, xylina, made from wool, growing on a shrub, called by some Xylon and by some Gossypium." There is no doubt but what this referred to cotton. Cotton was probably introduced into Europe by the Saracens and first manufactured in Spain in the early part of the 13th century. It was introduced into England by the Dutch, and the first mention made of it in trade appears in L. Roberts, "Treasury and Traffic," published in 1641, which says: "They buy cotton wool in England that comes from

---

[1] United States Pharmacopea, IX, 208.

[2] British Pharmacopea.

[3] Asvalayana Sranta Seitra.

Cyprus and Smyrna, and at home work the same and perfect it into velveteens, fustians, dimities, and such stuffs, where it is returned and sold in London."

It is interesting to note that cotton wool was used about 1250 in England for candle-wicks, though the extent of the industry is not recorded.[1] In the Western Hemisphere, the first voyage of Columbus to the West Indies in 1492 found cotton cultivated, and woven fabrics made from it being worn by the inhabitants. Cortes, in 1519, was presented with cotton garments by the natives of the Yacatan.[2] At the beginning of the 16th century the Mexicans used cotton garments to a large extent. In Peru, about the time of Pizarro's conquest in 1523, many of the inhabitants were clothed in cotton garments. This may be accounted for from the fact that cotton is indigenous to Peru. According to the historian Bancroft, the first attempt at cotton cultivation in the American Colonies was at Virginia in 1621.

It has been stated that the cotton plant was not actually grown as a fiber crop until the beginning of the 17th century,[3] and that until towards the close of the 18th century the methods employed in cultivation, treatment, etc., were empirical. The ginning process was carried out by primitive means and the daily output per man was less than 5 pounds of cotton. The simplest form of ginning machine was known as a Churka. It consisted essentially of two wooden rollers fixed in a rough frame, the top roller being usually stationary and the lower roller rotated by a handle. On passing the fibers of the seed cotton between the rollers the lint is drawn through, while the seed does not pass the rollers but falls to the ground. The fiber is uninjured by this simple type of machine.

The modern development of the cotton industry dates from 1792, when the saw-gin was patented by Eli Whitney, this invention considerably simplifying the ginning process. This epochmaking improvement in the early treatment of the cotton fiber

---

[1] Encyclopedia Britannica, 11th Ed. **7**, 281. For details of the fiber from different pickings of Egyptian cotton, see T. Kearney, Bur. Plant Ind., Circ. 110, 37; abst C. A. 1914, **8**, 1211.

[2] Encyclopedia Britannica, 11th Ed. **7**, 265.

[3] "Cotton and the Vegetable Fibers," E. Goulding and W. Dunstan, 49.

was as important from many considerations as the inventions of Arkwright and others with regard to textile manufacture. In 1787 at Beverly, Mass., the first mill for the production of cotton goods is stated to have been erected. In 1788 there were 143 water mills in the United Kingdom engaged in the cotton industry; of these mills, 41 were in Lancashire. About this period much attention was given to the question of cotton production. We find, for example, the East India Company making efforts to improve the growing of cotton in India. Unsuccessful endeavors were made to acclimatize exotic cottons,[1] best results being obtained by improving indigenous cotton plants. In 1790, one and one-half million pounds of cotton were produced in the United States; by 1800 the number of pounds had risen to 35 millions. In 1850 the figure was 1021 millions, while in 1918 it reached 7,950 millions.

Botany of Cotton. Long unicellular hairs envelop the capsule seeds in various species of the plants of the genus *Gossypium* belonging to the Mallow (*Malvaceae*) order, and, when freed from wax, fat, and other non-cellulose products, these hairs constitute the extremely important fiber known as cotton. The seed itself is usually covered with a coarse yellow or brownish hairy growth, whereas the cotton hair or down-like substance is many times longer and is also nearly colorless.

Cotton plants are usually perennial, but crops in other than the first or second year are generally poor, so that from an economic aspect the plants are considered as annuals. Yearly plants are also easier to cultivate, and insect and fungoid pests more readily combated.

With the opening of the flower buds,[2] white or yellow petals

---

[1] Encyclopedia Britannica, 11th Ed. **7**, 266.

[2] Monie ("The Cotton Fiber") gives the following description of the cultivation of the cotton plant: "The plant, although indigenous to almost all warm climates, is nevertheless only cultivated within a very limited area for commercial purposes, the principal centers of cotton agriculture being in Egypt, the southern portions of the United States, India, Brazil, the west and southern coasts of Africa, and the West India Islands. A large amount of white cotton is raised in China, but this is almost entirely used in the home manufactures. The time when sowing is begun in the several districts varies considerably, being largely dependent upon the climatic influences. The seasons, however, are generally as follows: American.—From the middle of March to the middle of April. Egyptian.—From the beginning of March to the end of April. Peruvian and Brazilian.—From the end of December to the end of April. Indian or Surat.—From May to the

generally appear and these darken in color for 3 to 4 days and then deciduate. The color of the flower varies generally with the different species. Upland American plants show a white or whitish yellow flower, from which are gradations in color to the purplish red of the cotton trees of India. When the petals and stamens separate, the young fruit calyx gradually increases and is known as a pod or boll.

This pod at first has a green color but on ripening turns brown. The surface of the boll gradually hardens and ridges are

---

beginning of August. In the various American plantations the sowing time begins and ends almost simultaneously, while in other countries, especially where the atmosphere and climate are subject to much variation, the period of planting fluctuates. The plants in some parts being several inches above the ground, while in other parts of the same country the fields may be only under preparation. When the sowing is finished and before, and some time after the crop makes its appearance, keeping the ground free from weeds is the main object to be looked to, otherwise the soil would become much impoverished, and the product would be an inferior quality. In from eight days to a fortnight after sowing, the young shoots first appear above the ground in the form of a hook, but in a few hours afterwards the seed end of the stalk or stem is raised out of the ground, disclosing two leaves folded over and closed together. The leaves and stems of these young plants are very smooth and oily and of a fleshy color and appearance, and, as before stated, extremely tender. In examining the cotton plant from time to time during its growth, some interesting and instructive objects will be observed. Firstly, in regard to the formation of the leaves, it will be found that they will vary in form in different parts of the stem, thus, for instance, on a Gallini Egyptian (*G. barbadense*) plant, the lower leaves were entire, the center or middle 3-lobed, while the upper leaves were 5-lobed. In the *G. hirsutum* species, the lower leaves have 5 and some 3 lobes, with the small branched petioles of a hairy nature, while the upper leaves are entire and undivided. In the Peruvian cotton plant, the lower leaves are entire and of an oval shape, while the upper leaves have 5 acuminated lobes. Another interesting point observable in the growth of the cotton plant is the presence of a small cavity situated at the lower end of the main vein of each leaf. Through this opening, on warm days, the plant discharges any excess of resinous matter which circulates through its branches. Before the plant attains its full height it begins to throw off flower-stalks which are generally (when perfectly formed) small in diameter and of considerable length; on the extremity of these stalks, the blossom pod after a time appears, encased in three leaf-sheaths or calyxes, with the fringes of various lengths. Gradually this pod expands until it attains to about the size of a bean, when it bursts and displays the blossom. This blossom only exists in full development for about twenty-four hours, when it begins to revolve imperceptibly on its axis and in about a day's time twists itself completely off. When the blossom has fallen, a small 3-, and in some cases, 5-celled triangular capsule or pod of a dark-green color is disclosed, which increases in size until it reaches that of a large filbert. Meanwhile the seeds and filaments have been in course of formation inside the pod, and when growth is completed the expansion of the fiber causes it to burst into sections, each cell of which, and adhering firmly to the seeds, is a tuft of the downy material." See also "Varieties of American Upland Cotton," F. Tyler, Bull. 163, U. S. Bureau Plant Industry, 1910, pp. 127, pl. 8, fig. 67.

formed on it, down the center of one of the ridges being a groove. As the white boll opens along this groove, the contents of the capsule spreads out, forming a white downy mass. The cotton fiber requires plenty of air and light for complete maturing. The mixed cotton and seeds are easily picked as soon as the boll is dry.[1]

Long staple cotton fiber has a length of $1^1/_4$ to 2 inches or more. In this class is Sea-Island and improved Upland American cotton. A medium staple such as Peruvian and Brazilian ranges from $^7/_8$–1 in., and a shorter staple $^3/_8$–$^3/_4$ in., representatives of this latter class being the cottons from India. In general, the whiter, cleaner, longer and more silky the individual fiber, or the smaller the diameter, the higher in commercial value as a textile does the cotton become. The longest staple and most highly prized variety is the "Sea-Island" cotton known as "long Georgia."

Cotton even of a definite species is influenced by many conditions and the length of fiber is not a constant. The following table gives lengths and diameters of various cotton fibers:

Place of Growth	Description of Cotton	Length of Staple (In Inches)		Diameter of Fiber (Inches)		Fraction (Mean)
		Min.	Max.	Min.	Max.	
United States	New Orleans..	0.88	1.16	0.00058	0.00097	$^1/_{1290}$
Sea Islands..	Long Stapled.	1.41	1.80	0.00046	0.00082	$^1/_{1562}$
S. America...	Brazilian......	1.03	1.31	0.00062	0.00096	$^1/_{1265}$
Egypt.......	Egyptian.....	1.30	1.52	0.00059	0.00072	$^1/_{1526}$
....	Indigenous or Native.....	0.77	1.02	0.000649	0.001040	$^1/_{1185}$
Indian.......	American Seed	0.95	1.21	0.000654	0.000996	$^1/_{1212}$
....	Sea Island or Egyptian...	1.36	1.65	0.000596	0.000864	$^1/_{1396}$

The isolated cotton fiber is a single elongated cell, broken roughly at the base from being torn from the seed, and terminating at the end in an elongated solid point. Upon magnification the fiber appears as a granular striped band, twisted spirally, thicker at the edges and containing a central canal without liquid, the

[1] "Cotton and Other Vegetable Fibers," E. Goulding and W. Dunstan, p. 12. For details of Caravonica cotton, see T. Hanausek, Chem. Ztg. Rep. 1910, **34**, 455; abst. J. Soc. Dyers Col. 1910, **26**, 251.

enveloping sheath being so far collapsed that the inner walls appear in contact. This becomes more noticeable upon moistening the fiber—a characteristic of cotton.[1]

Externally the fiber is enveloped in a thin skin called the cuticle, which substance differs chemically from cellulose, and has been regarded as a conversion product of the latter induced by moisture and air.[2]

According to F. Bowman[3] a typical cotton fiber when exam-

---

[1] A. Flatters has published a work (1906), "The Cotton Plant," on the microscopical development of the cotton fiber, accompanied by excellent photomicrographs of the various species of cotton, and different periods of the developing fiber. As the result of his investigations the following conclusions are arrived at: "1. That the cotton fiber is a cuticular outgrowth of the ovule. 2. That the fibers are not all developed at the same time, on the same ovule. 3. That the deposit of cellulose on the cell-wall of the fiber is not uniform and regular. 4. That the spiral twisting of the fiber is dependent upon the uniform deposit of cellulose, and subsequent evaporation of moisture and cuticular contraction. 5. That an average long-stapled fiber and an average short-stapled one have practically the same cavity-area for the deposit of cellulose. 6. That all fibers lacking spiral twisting are not necessarily unripe fibers, but fibers which may have attained solidity by continued deposit. 7. That the cotton fiber is made up of three primary elements—(*a*) the cuticular envelope; (*b*) the secondary deposit of cellulose; (*c*) the endochromic coloring matter. 8. That these primary elements are demonstrable by microscopic and chemical analysis."

[2] This spiral formation has been attributed to the fact that upon ripening, the juices in the fiber are drawn back into the plant or dry up, and in doing so cause the fiber to become twisted from the unequal contraction and collapse of the cell wall. It has been noticed that when fibers which have had a stunted or immature growth, usually either have no inner canal, or the canal has been stopped up. This is a decidedly inferior cotton. The fiber is weak, brittle, of reduced strength and durability. This inferiority is readily apparent in attempting to spin or to nitrate or acetate the fiber; the internal diameter being so much greater, and the absence of the inner canal, causes slower and more unequal penetration of acids, and more difficulty in washing the finished product free from contained acid. Such cotton is known in the trade as "dead."

It has been stated by Humboldt, that the most suitable section for the cultivation of the *Gossypium barbadense*, *G. arboreum*, and *G. hirsutum* is between the equator and the 34th degree of latitude, a mean yearly temperature of 68°–86° F. being required. *G. herbaceum* thrives best in those zones where the winter temperature does not fall below 50° F., nor rise above 77° F. in summer. In the United States the cotton plant is cultivated up to 38° latitude north, but the most desirable fiber is obtained along the eastern coast and in proximity to the ocean, between 25° and 33° north latitude.

[3] In the unripe fiber, the canal is filled with protoplasmic matter, but in the ripening of the plant this liquid dries up, and the walls of the tube collapse and flatten out. As the ripening process increases, the adhesion of the fiber to the seed decreases much in the same manner as the ripening of fruits, so that the ripe cotton is easily separated in the ginning process. In some species, this separation of hair from the seed is so perfect that after ginning the seed shows a polished black appearance, and is locally called

ined microscopically, shows (a) an outer cuticle or integument forming the skin of the fiber; (b) an inner tube attached to the outer cuticle consisting of cellulose and protoplasm, which forms the substance of the fiber; (c) an inner layer of a firmer deposit; and (d) a pith-like deposit containing coloring matter which may be present and existing in detached pieces or filling the central lumen.[1]

The plants of the Mallow order—to which the cotton belongs—and which include both herbs, shrubs and small trees, are from 3–20 feet high and have been cultivated for ages over a wide area. They are indigenous mainly to maritime tropical regions.[2] Under cultivation their range has been extended to approximately 40° either side of the equator (or to the isothermal line 60° F.).[3]

The botanical classification of cotton plants is difficult on

---

"black seed" cotton in distinction from the upland or "green seed" cotton. The length of the fiber, which varies considerably even among the same variety, will range from 2 inches (5 cm.) in the Egyptian to $^{3}/_{4}$ inch (18 mm.) in the inferior grades. (Structure of the Cotton Fiber, 19) gives the diameter of the fiber as 0.0004–0.0016 inch.

The central cavity known as the lumen is generally small in comparison with the diameter of the cell walls, the thickness of the latter being of considerable importance in the speed of acid penetration in nitrating processes. Sometimes the lumen is several times as broad as the cell wall. Such a cotton will both nitrate readily, wash easily, and sustain considerable mechanical loss in the several processes of treatment.

[1] Whereas cellulose is readily soluble in ammoniacal cupric oxide solution, and also in concentrated sulfuric acid, cuticle is difficultly so. In treating cotton fiber with either of these reagents, a peculiar phenomenon is observed. The cotton swells up, but the cuticle is not visibly affected. As the bast fibers contain no cuticle, they do not exhibit this reaction, which therefore is a method of differentiation between the two classes of fibers.

In commerce there are 8 different degrees of fineness in cotton recognized, varying in diameter from 0.004–0.008 inch. The oil extracted from raw cotton appears to be very similar to, if not identical with, cottonseed oil, and has been supposed to have been carried up the fiber from the seed itself.

[2] The "count" of cotton is a term applied to the number of hanks of 840 yards each contained in 1 pound. Size 60's, for instance, means that 60 hanks, each 840 yards in length, will weigh 1 pound. The English system of numbering, used mostly in England, United States, India, Switzerland, Germany, includes designation of twisted as well as single yarns. For instance, if 2 single threads of count 60 are twisted together, this would be designated at 2–60's. The Belgium system is to use the number 840-yard hanks in 500 grams; that of the French is based on the decimal system, the count being the number of 1000-meter length hanks required to weigh 500 grams. In Austria, the method is to count the number of hanks of 950 cells each in 500 grams. According to the number of the twisted threads, there is a decrease in length of 2%–6% in twisting with an increase in diameter.

[3] The following description of the typical cotton plant is abstracted from Bulletin 33, U. S. Department of Agriculture. "The cotton plant belongs to the *Malvaceae*, or mallow family, and is known under the generic

account of several considerations. The plants of this genus respond readily and are influenced by intensive cultivation and selection, and with variations in environment, climate and soil, and easily undergo hybridization. The large interchange of seeds between different countries has naturally greatly altered the distinctive characteristics of the individual species.

Of the large number of species of the *Gossypium* genus[1]

---

name *Gossypium*. It is indigenous principally to the islands and maritime regions of the tropics, but under cultivation its range has been extended to 40° or more either side of the equator, or to the isothermal line of 60° F.

In the U. S., latitude 37° N. about represents the limit of economic growth. The *Gossypium* plant is herbaceous, shrubby, or arborescent, perennial, but in cultivation herabceous annual or biennial, often hairy, with long, simple, or slightly branched hairs, or soft and tomentose, or hirsute, or all the pubescence short and stellate, rarely smooth throughout; stem, branches, petiolate; peduncles, leaves, involucre; corolla, ovary, style, capsule, and sometimes the cotyledons more or less covered with small black spots or glands. Roots, tap-rooted, branching, long, and penetrating the soil deeply. Stems erect, terete, with dark-colored ash-red or red bark and white wood, branching or spreading widely. Branches terete or somewhat angled, erect or spreading, or in cultivation sometimes very short. Leaves alternate, petioled, cordate, or subcordate, 3- to 7-, or rarely, 9-lobed, occasionally some of the lower and upper ones entire, 3- to 7-veined. Veins branching and netted; the mid vein and sometimes adjacent ones bear a gland one-third or less the distance from their bases, or glands may be wholly absent. Stipules in pairs, linear-lanceolate, acuminate, often ceduous. Flowers pedunculate. Peduncles subangular or angular, often thickened towards the ends, short or very short, erect or spreading; the fruit is sometimes pendulous, sometimes gladular, bearing a leafy involucre. Involucre 3-leaved or in cultivation sometimes 4-; bracteoles often large, cordate, erect, appressed, or spreading at summit, sometimes coalescent at base or adnate to calyx, dentate, or lancinate, sometimes entire or nearly so, rarely linear; calyx short, cup-shaped, truncate, shortly 5-dentate or more or less 5-parted. Corolla hypogynous. Petals 5, often coalescent at base and by their claws adnate to the lower part of stamen tube, obovate, more or less unequally transversely dilated at summit, convulute in bud. Staminal column dilated at base, arched, surrounding the ovary, naked below, above narrowed, and bearing the anthers. Filaments numerous, filiform, simple or branched, conspicuous. Anthers reniform, 1-celled, dehiscent by a semicircular opening into two halves. Ovary sessile, simple, 3- to 5-celled. Ovules few or many, in two series. Style clavate, 3- to 5-parted; divisions sometimes erect, sometimes twisted and adhering together, channeled, and bearing the stigmas. Capsule more or less thickened, lethery, oval, ovate-acuminate, subglobose, mucronate, loculicidally dehiscent by 1 to 5 valves. Seed numerous, subglobose, ovate of subovate, oblong or angular, densely covered with cotton or rarely glabrous. Fiber sometimes of two kinds, one short and closely adherent to the seed, the other longer, more or less silky, of single, simple, flattened cells, more or less spirally twisted, more readily separable from the seed. Albumen thin, membranous or none. Cotyledons pilcate, auriculate at base, enveloping the straight radical."

[1] A. Henckel (Bull. Bur. Plant Ind. (U. S.) 1909, No. 139, pp. 40) has presented an unusually good illustrated description of *Gossypium* species. See H. Rusby, Pharm. Era, 1909, **42**, 634. F. Tyler, Bull. No. 163, Bur. Plant Ind. (U. S.) 1910, pp. 127. For interesting description of the methods used in the maintenance of the quality of Egyptian cotton, see G. Dudgeon, Bull. Imper. Inst. June 1918, 160–170.

known, only about 20 are cultivated. Their principal habitats are North America and India, although the species is more or less indigenous to all sub-tropical countries. A. Todaro records 52 distinct species. The Index Kewensis gives 42 species and 88 synonyms. However, only about twenty species are cultivated. A much smaller number than this (4 or 5), however, are of extensive economic importance, among which may be mentioned the following:

Gossypium herbaceum (Linn.) or *Gossypium hirsutum* (Linn.). The distinction between these two species is indefinite. The first is considered to be indigenous to Asiatic Turkey (Smyrna cotton) —also known as *G. indicum.* In localities where other varieties of cotton cannot be grown with profit, this variety is cultivated in America, Egypt and China and produces a short, relatively coarse fiber often called Surat or Indian cotton. The staple, however, is very strong.

G. hirsutum is regarded as indicative of the extremely important upland cottons of the United States of America, and the cotton of Texas and New Orleans. According to Watt, the upland cottons are to be more properly regarded as made up of various hybrid forms between *G. hirsutum* and *G. mexicanum,* the plants of these species being very hardy and attaining a height of 7–8 feet.

Gossypium barbadense (Linn). This species includes the highly prized, silky haired, Sea Island cotton, although again according to some authorities, this variety is more properly considered a hybrid, and allied to *G. vitifolium.* It has a yellow flower and small, black, smooth seeds. This most valuable cotton, which is native to West Indies, produces the "finest staple" cotton and is only obtained by cultivation. This species yields not only the very strong, long fiber, but yields a lower percentage of lint and inferior fibers than any other variety of cotton. The individual fibers are very fine, with numerous uniform twists and it has a lustrous creamy color. In consequence, its net value in spinning and thread manufacture is correspondingly enhanced, while it produces an extremely fine yarn,[1] being largely used for

---

[1] Monie, "Structure of the Cotton Fiber," p. 40. For earlier analyses of the composition of crude cotton, see C. Schmidt and Hecker, J. prakt. chem. 1847, **40**, 257; Poly. Centr. 1847, **13**, 36; Jahr. Chem. 1847–1848, **1**, 1130.

the finer numbers of thread and yarns. Its cultivation to greatest perfection is in regions where there is a hot moist atmosphere combined with a heavy rainfall. Consequently it is found at its best near the sea in tropical countries, such as off the coast of Georgia, South Carolina and Florida, although that grown in Jamaica and in some of the West Indies—due to adverse climatic conditions—is of a rather inferior grade. It is grown also in Egypt, where it has been claimed this species to be of African origin.[1] Watt considers some Egyptian cottons to be hybrids of *G. peruvianum* (Engler).

Gossypium brasiliense (Macf.) and *G. peruvianum* (Engler) are related tropical species native of South America, being cultivated mainly in Brazil and Peru. The plants are 10–15 feet in height and bear a yellow flower. The pods, which usually contain 8–10 black seeds, each yield a long staple of great tensile strength, although a somewhat coarse fiber, which is perhaps next in value to Sea Island cotton. Most of the fibers are only partly twisted. This cotton usually has a light creamy color. The hair is readily separated from the seeds but the latter are grouped together, adhering in clusters. The fiber is known by the term "kidney cotton." Usually the commercial cottons contain much immaturely developed and short fiber product as well as a large amount of foreign matter such as broken leaf, sand, seeds, etc.

Gossypium arboreum (Linn.) represents a species from which Indian cottons are derived. *G. neglectum*, *G. herbaceum* (Linn.), *G. obtusifolium*, *G. wightianum* and other species are also considered to represent some Indian cottons. *G. arboreum* is really a large shrub or a small tree rising to a height of 15–20 feet. It produces only a relatively small proportion of fiber, and is not very extensively cultivated.

Gossypium religiosum (*G. chinese* (Fisch) and (Otto)) represents a type of cotton plant from China and Siam. It yields the so-called yellow "nankin" cotton. It is not, however, of especial commercial significance, and is probably related to the *G. arboreum*.

F. Parlatore[2] also includes *G. tahitense*, which flourishes in the Pacific Islands, and *G. sanwichense* which occurs in the Hawaiian, among the commercial cottons. These last two species

---

1. Masters, J. Linn. Soc. **19**, 213.
2. See F. Parlatore, "*Le specie dei cotoni*," 1866.

may, with propriety, be included under *G. barbadense* and *G. hirsutum.*

Commercial cottons may also be classified into two groups (1) and (2) with various sub-sections, as follows:

(1) Seeds covered with long hairs only, flowers yellow, turning to red.
  (A) Seeds separate, as *G. barnadense* (Linn.).
  (B) Seeds of each loculus united, as *G. brasiliense* (Macf.).
(2) Seeds covered with short hairs.
  (A) Flowers yellow or white, turning red.[1]
    (a) Leaves 3 to 5 lobed, often large, flowers yellow, às *G. hirsutum* (Linn.).
    (b) Leaves 3 to 5, seldom 7, lobed, small, flowers yellow, as *G. herbaceum* (Linn.).
  (B) Flowers purple or red, leaves 3 to 5 lobed, as *G. arboreum* (Linn.).

Bombax cotton is a species of fiber quite similar to that of the cotton plant, having been collected for centuries from various

---

[1] A. Perkin, J. C. S. 1916, **109**, 145; abst. C. A. 1916, **10**, 1326. He has made an attempt to ascertain if there *is any chemical distinction* not only *between the Egyptian* and ordinary Indian yellow cotton flower, *Gossypium herbaceum*, but also between these and the red, pink, and colorless petals of other varieties; also whether the red coloring matter in the red and yellow flowers is due to the red oxidation products of either gossypetin or gossypitrin. Red cotton flowers, *G. arboreum*, Linn.: The red alcoholic extract of 1600 gm. flowers was concentrated, diluted with hot water, and the alcohol evaporated off. After extraction with ether the liquid was boiled with lead acetate solution and the greenish brown precipitate decomposed with H_2S. Filtration of the maroon liquid and evaporation *in vacuo* for several days gave a red, semi-gelatinous product from which was isolated isoquercetin. Other flavone glucosides could not be detected, thus showing a marked difference from the yellow Egyptian flowers. The red, viscous mass obtained by concentrating *in vacuo* the filtrate from the isoquercitrin did not yield the typical color reactions of gossypitone after hydrolysis with boiling 1% H_2SO_4 and removal of quercetin by dissolving in pyridine and precipitating with ether, repeating the process, indicating that the color may be due rather to a true anthocyanin. Yellow flowers, *G. neglectum:* the concentrated alcoholic extract, on long keeping, gradually gave a precipitate which, dissolved in hot water, treated with lead acetate solution, decomposed with H_2S, and concentrated *in vacuo*, gave a semi-gelatinous mass, which, recrystallized first from dilute alcohol, then from boiling water, yielded gossypitrin m. 240°-242°, whereas the (*A*) isolated from the Egyptian flowers (*loc. cit.*) m. 200°-202°. It was found that by boiling the higher m. variety with acetone, finer needles with 1H_2O were formed, and that these m. 200°-202° whether anhydrous or not. This form is converted into the higher m. variety by boiling with water. The mother liquors from the crude (*A*), on further evaporation *in vacuo*, gave a small amount of a soluble glucoside which yielded quercetin on hydrolysis, while the final mother liquors contained a readily soluble quercetin glucoside, from which, by the methods

fruit capsules of the Bombax family which are closely allied to the *Malvaceae* (cotton family), and has found commercial uses. This form of cotton is variously known as "vegetable down," and "vegetable edredon."

Bombax cotton comprises soft fibers possessing considerable luster, and white to yellow in color. Like cotton, they are seed hairs, and therefore are morphologically similar. There is an entire absence of spiral twist, the fibers being shorter and the cell walls decreased in thickness, all of which tends to the production of diminished tensile strength. This form of cotton finds its principal uses in wadding for upholstery work, being too weak for spinning. When nitrated this cotton forms a nitrocellulose of ready solubility and fluidity.

Of the cotton grown in the United States, the Sea Island variety is the longest and finest cotton produced in the world, being soft and silky and possessing an excellent luster. This cotton is cultivated chiefly in the Sea Islands off South Carolina, and in the interior of Georgia and Florida, and is also extensively cultivated in the West Indies. In order to maintain the quality of Sea Island cotton, it is necessary that careful seed selection be practiced, or the strain will deteriorate in quality.

Inasmuch as the plant is more delicate than other varieties, it requires special treatment during growth, and especial attention is placed on the question of fertilization. It thrives best in a rather sandy soil and highly humid atmosphere. Inasmuch as Georgia and Florida also grow considerable quantities of Up-

described for the red flowers, was finally separated a small amount of a red powder very similar to that isolated from the *G. arboreum*. The filtrate from the lead precipitate, treated with basic lead acetate, gave a precipitate which yielded isoquercitrin when decomposed as usual. The ordinary yellow Indian cotton flower, *G. herbaceum*, gave the same results as the *G. neglectum*, the surprising feature being *the absence of quercimeritrin, an important constituent of the Egyptian yellow flowers.* The white and pink Indian flowers yielded no definite results. Like gossypetin, (*A*) and $O:C_6H_4:O$ in alcohol when gently warmed, yielded maroon needles of *gossypitrone*, $C_{21}H_{18}O_{13}$, gradually decomposed above 200°, m. about 255°–259°, dyes Al-mordanted cotton green. Like the red cotton petals, it gives a greenish brown precipitate with lead acetate. The ease with which it is reduced to (*A*) by SO_2 indicates that it is the quinone of (*A*). On wool the shades were identical with those produced by (*A*), thus showing the reverse properties of those of gossypetin and its quinone. Heated to boiling with 7% H_2SO_4 it is both hydrolyzed and reduced, the main product being apparently gossypetin; this is an important difference from the behavior of the red product obtained above from the red petals, indicating that the two are not identical.

land cotton, great care must be exercised to guard against deterioration of the Sea Island cottons by means of hybridization induced by insect cross fertilization. It has been found expedient to frequently obtain new seed from the coast districts. Sea Island cotton is seldom if ever used for nitration, being employed in commerce for spinning only the finest and best yarns.

The American Upland cottons are grown to a much larger extent than the other varieties, being used in the manufacture of yarns of medium quality. Of this cotton, the United States annually produces something like three million tons—approximately two-thirds of the world's production of this commodity. The seeds are usually covered with fuzz or down, differing in this respect from the seeds of the Sea Island variety, which are smooth and black. This down is used extensively for nitration in the manufacture of smokeless powder, pyroxylin lacquers, artificial leather and bronzing fluids.

Microscopy of Cotton. The individual cotton filament is a flattened, hollow, unicellular cell of ribbon-like form, or a collapsible tube twisted a number of times, closed at the apex to form a point, and without transverse partitions. The central canal is comparatively large and runs nearly to the apex of the fiber, the seed walls being membraneous. As the hair ripens, it loses its cylindrical form and becomes more or less flattened, and then appears as a narrow, somewhat opaque ribbon or band with slightly thickened rounded edges. The cotton fiber, like all seed hairs, naturally has but one end closed, the other being broken off at the point of attachment.[1] The outer wall is covered with

[1] The twist in cotton fiber is not present in the early stages, but only becomes developed after the boll has opened and the cotton has been exposed to both light and air. These twists do not represent complete revolutions of the fiber on its central axis, some being right-handed, and others in the opposite direction. They occur at irregular distances from one another, and vary greatly in the degree of convolution. There is great variation in the number of twists in a given length of fiber, being increased by the care exercised in cultivation. The number of twists vary directly with the fineness of the fiber, and hence are most numerous per given length in Sea Island cotton. It is a peculiarity that the presence of the twist imparts a roughness to the fibers which apparently enables them to exert a certain amount of grip on one another, thus facilitating their spinning. Unripe cotton is comprised of thin, immature, transparent filaments, possessing little or no twist, and are technically known as dead fibers. They acetate and nitrate with difficulty, and yield cellulose esters which are not readily stabilized. For this and other reasons, the presence of much immature cotton reduces the commercial value of the product.

a waxy substance,—cutin (cuticular cellulose)—while dried-up residues of protoplasm and cholesterin coat the wall of the central canal. The peculiar swelling of the cellulose and bursting, coupled with the partial breaking away of the cuticle under the action of cuprammonium has been described by Wiesner. The protoplasmic inner wall, like the cuticle, also resists the solvent action of this reagent. R. Haller[1] has observed that both the cuticle and protoplasmic layer resists the severe alkaline treatments of the industrial bleaching processes, at all events in a great majority of the fibers. The canal and protoplasmic layers readily absorb basic dyestuffs such as safranine, and retain the color when washed with boiling alcohol, whereas the cellulose remains unchanged. The retention of dyestuff under these conditions is considerable in the case of raw cotton, but decreases in proportion as the waxy material is removed; in all cases, however, the cellulose itself remains substantially colorless. The cutin of the cuticular celluloses is completely removed by treatment for half an hour with a caustic soda solution of mercerizing strength. When a mercerized fiber is dyed with a substantive or direct dyeing dyestuff, the cellulose itself is deeply colored, and on treatment with cuprammonium it then swells uniformly and ultimately dissolves, leaving the protoplasmic wall of the central canal as a translucent colored line. The unmercerized fiber, when similarly dyed and treated with cuprammonium, exhibits a strongly colored cuticle and lumen and only a slightly colored cellulose. It would appear from the investigations of Haller that the cuticle and protoplasmic wall of the lumen, besides possessing a mordanting property towards basic dyestuffs, constitute layers which also exercise a strong affinity for substantive dyestuffs, and which, being penetrated by these dyestuffs, only with difficulty hinder the access of the color to the cellulose between them. In this manner the author endeavors to explain the darker shades obtained with substantive dyestuffs on mercerized fibers deprived of their cutin, whereas unmercerized cotton fiber when treated with cuprammonium and then washed, and dyed with a sub-

---

[1] Zts. Farben Ind. 1907, **6**, 125; abst. J. S. C. I. 1907, **26**, 523; Chem. Zentr. 1907, **78**, II, 953; 1908, **79**, II, 1139; Jahr. Chem. 1905–1908, II, 3185; Wag. Jahr. 1908, **54**, II, 376; Zts. ang. Chem. 1907, **20**, 2085; 1908, **21**, 267. See also R. Haller, Text. u. Farben Ztg. **14**, 221; abst. C. A. 1907, **1**, 2495; Chem. Ztg. 1908, **32**, 838; abst. Meyer Jahr. Chem. 1908' **18**, 505.

stantive dyestuff, it is found that those portions from which the cuticle has broken away are intensely colored, while those parts which are still protected by the cuticular layer are only slightly stained. Cuprammonium swells and dissolves the cellulose and leaves the cuticular cellulose unchanged in the form of flax, whereas strong alkaline solutions dissolve not only the cutin from the cuticular cellulose, leaving the cellulose portion of the cuticle as part of the normal cellulose of the fiber.

The microscopic characteristics of the cotton filament are so pronounced as to readily differentiate it from all other naturally occurring fibers. As stated, it exhibits the appearance of a flat, ribbon-like band, more or less twisted on its longitudinal axis, the edges of the fiber, however, being somewhat thicker and usually presenting irregular corrugations. At times, however, the filament presents the appearance of a smooth, flat band, with little or no thickening at the periphery. It is a peculiar fact that the twisted fiber does not appear to be continuous in any one direction, it having been observed that the fiber may be not only twisted axially to the right, naturally then exhibiting a flattened portion without any twist at all, but may also show an axial twist to the left. It would appear that the twist of the cotton fiber is a phenomenon coincident through cultivation, and is not possessed,—at least in so noticeable a degree,—by wild cotton.

According to Monie,[1] the rotary motion begins with the process of vacuation in the fiber, and this, in turn, is caused by the withdrawal of some of the fluid in the fiber when the seed begins to ripen, and as this is effected slowly and progressively, commencing at the extremity farthest from the seed, i. e., the apex, gradually receding toward the base, the free end or opened apex, twists on its own axis several times, thus producing the convolute form shown under the microscope.

According to Hanausek,[2] with the increase in the number of fiber twists in a given length of fiber, the greater is the regularity of these twists, and correspondingly is the commercial value of the cotton enhanced.

Herbig[3] takes exception to this statement. In general, however, for about three-quarters of its length, the fiber maintains

1. "The Cotton Fibre," page 25.
2. "Microscopy of Technical Products," page 61.
3. Zts. ges. Text. Ind. 1900, 17.

a comparatively uniform twist, then gradually tapers to a point, which point is not only perfectly cylindrical but usually solid. In some instances, portions of the fiber may exhibit cylindrical and apparently solid spaces, which doubtless are caused by irregularities in the growth of the cell. At such places the strength of the fiber is materially weakened and will not absorb solutions with the same avidity or to the same degree as the balance of the filament. The cell wall is comparatively thin, the lumen occupying about two-thirds of the entire breadth. Between its thickened edges the fiber under the microscope appears finely granular and occasionally the surface is reticulated. Fibers of dead cotton, or those which are immature, are seldom twisted spirally and do not have a lumen, but appear as thin transparent or translucent bands. Unripe cotton or immature cotton, therefore, has a decreased value for purposes of manufacture, as it contracts and curls up in the warm atmosphere and high humidity of the mill, and consequently, yarn containing much unripe fibers depreciates considerably.

J. Matthews[1] has divided cotton fibers, from a microscopical viewpoint, into the four following classes:

(a) Those fibers which exhibit a smooth, straight, flat appearance with no suggestion of internal structure. These include immature cotton fibers and also filaments which have been overripe. The external wall, in general, of such fibers, is very thin.

(b) Filaments exhibiting a normal appearance through some portions of their length and in other parts a structureless appearance as in "a" above. These are termed "kempy" fibers; the solid tubular portion of which is particularly resistant to the absorption of liquids and dyestuffs and consequently remain uncolored or are imperfectly colored, while the rest of the fiber is dyed.

(c) Straight, tubular fibers, exhibiting a well-defined internal structure and a transparent cell wall of varying thickness. Fibers of this character, under the microscope, have some of the morphological appearance of linen, especially where the cell wall is thick. The fibers of *Gossypium conglomeratum* are especially liable to show this form.

(d) Normal structure of twisted band-like form. In cross-

---

[1] "The Textile Fibres," page 248.

section, the immature fibers exhibit only a single line with little or no structure and but slight indication of an internal opening.

The mature fiber is thicker in cross-section and usually exhibits a central opening. The main charcteristic of the microchemical reactions for cotton is that with cuprammonium solution previouly mentioned, cotton which has been bleached often indicates the external cuticle to be absent, and hence such a fiber may show but little or no distinction.

With iodine and sulfuric acid the cotton fiber becomes blue in color, although the cuticle usually remains colorless. Tincture of madder, gamboge, and dragon's blood, give an orange color; magenta produces a red color, distroyed upon the application of ammonia. The latter test serves as a chemical distinction between cotton and linen, provided the linen is unbleached, as flax does not show this latter reaction to an appreciable extent. With cotton filaments, anhydrous stannic chloride gives a black color.

E. Stanford and E. Viehoever[1] have recently minutely described the location and structure of the various glands of Upland cotton (*Gossypium hirsutum*).[2]

Anatomical Structure of the Cotton Fiber. The individual cotton filament appears to consist structurally of four distinct parts as observed from its behavior with a solution of ammoniacal copper oxide, and under the microscope is observed to swell without uniformity, there appearing at regular intervals annular sections upon which the cuprammonium appears to act only superficially, the result being that such fibers assume the form of a distended tube constructed at irregular intervals somewhat after the manner of string of sausages.

Höhnel believes these ligatures are merely portions of the cuticle, and explains their formation upon the assumption that the fiber swells so considerably as to rupture the undisturbed cuticle which, in places, adheres to the fiber in the form of irregu-

---

[1] J. Agric. Research, 1918, **13**, 419; abst. J. S. C. I. 1918, **37**, 460-A. See also A. Viehoever, L. Chernoff and C. Johns, J. Agric. Res. 1918, **13**, 345; abst. J. S. C. I. 1918, **37**, 485-A; C. A. 1918, **12**, 1562.

[2] The glands exposed to light were found to be surrounded by an anthocyan-bearing envelope of flattened cells and to contain quercetin, "probably partly or wholly in the form of its glucosides quercimeritrin or isoquercitrin," together with ethereal oil, resins, and perhaps tannins while the glands not exposed to the light were found to contain gossypol but no anthocyans. A table is given showing the microchemical reactions of the secretions of the internal glands and substances isolated from them.

lar patches visible under the microscope only with difficulty by reflected light, but readily so upon the interposition of a nicol prism. Occasionally the rupture is observed to occur obliquely in respect to the length of the fiber, in which instance the cuticle becomes drawn together in annular bands surrounding the periphery, while between these rings the greatly distended cellular portions protrude in the form of globules. With bleached cotton the cuticle may be almost entirely obliterated, and such fibers will, therefore, not exhibit the characteristic appearance above outlined. When the fiber has become greatly swollen by the action of the reagent it soon begins to pass into solution, whereupon the walls of the central canal appear quite prominently. The dissolving action proceeds with great rapidity; however, there is a cuticular tissue surrounding the fiber which resists the action of the solvent for a much longer period than the inner parenchymetous portion. The four structural parts thus made, observed by the treatment with the reagents are:

(a) The main protoplasmic cell wall consisting primarily of pure cellulose and rapidly and readily completely soluble in the cuprammonium reagent;

(b) An external cuticula, perhaps slight sclerenchymetous, of a modified cellulose, much more resistant to the action of the reagent;

(c) The central canal wall containing fatty, waxy and cholesterol-like bodies which resist the reagent of the solvent much more energetically than the cuticula;

(d) The annular ligatures which surround the fiber at irregular intervals and which persist even after the canal walls have been obliterated by solution.

Butterworth has examined cotton fiber after treatment with cuprammonium solution under high magnification (from 1200 to 1600 diameters), and has observed spiral threads which apparently cross and tightly bind around the fiber at irregular distances, as well as spiral threads which pass from one structure to another, the core of the fiber exhibiting a spiral form which, in cross-section, appears to be made up of concentric rings.

Upon immature or unripe fibers, cuprammonium solution has a greater solvent action, such fibers exhibiting no structural differences. The tubular-shaped fibers, in general, swell greatly and finally dissolve without any appreciable structural modifications except that the usual inner core is left. Examination with a mega-microscope, under the highest magnification, has not resulted in indicating any cellular structure pertaining to cellulosic contents of the cellular fiber. M. Fort[1] has dealt with the details of the destructive breakdown of cotton under the process of beetling, and C. Cross and E. Bevan[2] have examined a sample of powdered cellulose thus produced. The sample was found non-reactive towards polarized light in comparison with the original cotton fibers; the hygroscopic moisture 5%–6%; formula of the dry product $C_6H_{10}O_5$; and treatment with 17.5% NaOH solution gave indications of a decided modification, yielding 40%–56% of the soluble forms of cellulose (α- and γ-celluloses), a large proportion of which was precipitable on acidification. The product showed many analogies with the starches in behavior.[3]

Dimensions of Individual Cotton Fibers. According to the United States Department of Agriculture Bulletin No. 33, the following table compiled by them from numerous measurements

---

[1] J. Soc. Dyers Col. 1918, **34**, 9; abst C. A. 1918, **12**, 2694; J. S. C. I. 1918, **37**, 121-A; Ann. Rept. Soc. Chem. Ind. 1918, **3**, 161.

[2] J. Soc. Dyers Col. 1918, **34**, 215; abst. C. A. 1919, **13**, 910; J. S. C. I. 1919, **38**, 7-A. C. Cross, J. Soc. Dyers, 1919, **35**, 271, found in this treatment considerable heat was developed up to a maximum temperature of 200°. The following results were obtained on examination of the fiber under the action of sodium hydroxide solution of 17.5% concentration. Original cotton: α-cellulose, 99.7%; β-cellulose, 0.8%. Half-tendered portion: α-cellulose, 92.3%; β-cellulose, 4.9%; hygroscopic moisture, 3.6%. Fully tendered portion: α-cellulose, 78.0%; β-cellulose, 16.2%; hygroscopic mixture, 3.3%. The results show that the destroyed fiber was not identical with the fine powder previously described.

[3] R. Haller (Chem. Ztg. 1908, **32**, 838; abst. C. A. 1909, **3**, 489; J. S. C. I. 1908, **27**, 976; Bull. Soc. Chim. 1909, **6**, 479; Chem. Zentr. 1908, **79**, II, 1138; Meyer Jahr. Chem. 1908, **18**, 505; Wag. Jahr. 1908, **54**, II, 376; Zts. ang. Chem. 1908, **21**, 2556. See also Zts. Farben Ind. 1907, **6**, 125, 127. J. Soc. Dyers Col. 1907, **23**, 167) has recorded observations made on ripe and unripe fibers obtained from *Gossypium arboreum*. He describes the "dead cotton" as ribbon-shaped with many indentations, distinct stripes and granular appearance. The interior appears full of a deposit. Ammoniacal cuprous oxide causes only a swelling and the indentations disappear. Considerable time is required to dissolve the fibers and the very young fibers seem to be totally unaffected by this reagent. The change of color from yellow to dark blue which is observed when $ZnCl_2$-I solution is applied takes place more quickly with the ripe than with the dead cotton. A solution of I in KI colors dead cotton a pale yellow; ripe cotton, yellow to brown. Under the microscope it is seen that only the contents (protoplasm) of the dead fibers is colored. An 18% solution of NaOH mercerizes ripe cotton as usual while dead cotton retains its shape and becomes more transparent. The lumen and contents almost disappear. Examined in a ray of polarized light the dead fibers appear non-luminous in a dark field (i. e., no double

taken, coveringa period of years, shows the maximum, minimum and and average length of some of the more important varieties of cotton:

Variety	Length in Inches			Diameter Inches
	Maximum	Minimum	Average	
Sea-island	1.80	1.41	1.61	0.000640
New Orleans	1.16	0.88	1.02	0.000775
Texas	1.12	0.87	1.00	0.000763
Upland	1.06	0.81	0.93	0.000763
Egyptian	1.52	1.30	1.41	0.000655
Brazilian	1.31	1.03	1.17	0.000790
Indian varieties:				
Native	1.02	0.97	0.89	0.000844
American seed	1.21	0.95	1.08	0.000825
Sea-island seed	1.65	1.36	1.50	0.000730

The varieties and qualities of cotton met with in commerce and all suitable for nitration, according to Hannan, are as follows:[1]

refraction), the ripe fibers under the same conditions show up brightly. The small affinity of dead cotton for dye-stuffs may be confirmed by dyeing in an indigo vat. However, in the case of the substantive dyes the dead cotton seems to have a much greater affinity than the ripe cotton. If dead cotton be mordanted with tannin and tartar emetic and then dyed in methylene blue only the cell contents will be colored. By treating such fibers with Schweizer's solution the difference in color of the contents and cell wall is more noticeable. The peculiar properties of dead cotton seem to point to an abnormal composition of the cell membrane.

M. Adam, Can. P. 170435, 1916. R. Adler, D. R. P. 314311, 1914; abst. J. S. C. I. 1920, **39**, 60-A. J. Aktschourin, Norw. P. 22900; abst. Chem. Ztg. 1913, **37**, 244. C. Almy, U. S. P. 1191142. M. Althausse, U. S. P. 679203, 679204, 1901; E. P. 19039, 1900; F. P. 304723; D. R. P. 123121. E. Asker, Pap. Fabrikant, **16**, 133; abst. Chem. Zentr. 1918, **89**, II, 161; C. A. 1920, **14**, 345. F. Barrett, J. S. C. I. 1920, **39**, 81-T. E. Berl, F. P. 454753, 1913; D. R. P. Anm. B-67713; abst. Chem. Ztg. 1913, **37**, 142. E. Becker, Pap. Fabrikant, 1919, **17**, 1325; abst. C. A. 1920, **14**, 837. R. Blochmann, D. R. P. Anm. 68060; abst. Chem. Ztg. 1913, **37**, 245. C. Braun, E. P. 137831, 1920. D. Brauns, Proc. Roy. Acad. Amsterdam, Sec. Sci. 1908, **10**, (2), 563; abst. C. A. 1909, **3**, 318. S. Born and J. Nelson, J. A. C. S. 1915, **37**, 1763; abst. J. S. C. I. 1915, **34**, 845; C. A. 1915, **9**, 2249. See C. A. 1914, **8**, 1435. A. Börner, E. P. 16262, 1904. B. Bull, J. C. S. 1897, **71**, 1090; abst. Chem. News, 1897, **76**, 249; Chem. Centr. 1897, **68**, II, 733; Jahr. Chem. 1897, **50**, 1507; Meyer Jahr. Chem. 1897, **7**, 151. Burgess Sulphite Fiber Co., Can. P. 161395, 162161, 162163, 1915. C. Clerc, E. P. Appl. 1965, 1918. L. Collardon, Can. P. 161932, 1915. Compagnie Francaise des Applications de la Cellulose, Swiss P. 57951, 1911. J. Cottin and J. Four, Belg. P. 251556; abst. Chem. Ztg. 1913, **37**, 245. C. Cross, J. S. C. I. 1920, **39**, 124-R. C. Cross and E. Bevan, J. C. S. 1918, **113**, 182; abst. C. A. 1918, **12**, 1380. J. DeCew, Can. P. 170723, 1916. P. and C. Depoully, and la Societe C. Garnier and F. Voland, E. P. 8642, 1884. V. Drewsen, U. S. P. 1283113, 1918; 1298479, 1298480, 1298481, 1919.

[1] This table is taken, with the kind permission of the author, Dr. J. Merritt Matthews, from "The Textile Fibres."

Types	Variety	L'gth Ins.	Diameter, Inches	Counts	Use	Properties
Sea-island...	Edisto......	2.20	.00063	300–400	Warp or weft	Long, fine silky, and of uniform diameter
	Florida......	1.85	.00063	150–300	do.	Shorter, but similar to above
	Fiji.........	1.75	.00063	100–250	do.	Less uniform in length, but silky and cohesive
	Tahiti.......	1.80	.00063	100–250	do.	Good, fine, and glossy staple
Egyptian....	Brown.......	1.50	.00070	120–down	do.	Long, strong, highly endochromatic
	Gallini.......	1.60	.00066	250–down	Warp	High-class staple of good strength
	Menouffieh....	1.50	.00066	200–down	Weft	Of good staple and luster
	Mitafifi......	1.25	.00066	100	Warp or weft	Fairly good staple
	White.......	1.00	.00078	70	do.	Pearly white, good long staple
Peruvian....	Rough.......	1.25	.00078	50–70	Warp	Strong, woolly, and harsh staple
	Smooth......	1.00	.00078	50–70	Weft	Less woolly and softer staple
	Red.........	1.25	.00078	40–50	Warp	Color weaker and harsher than brown Egyptian
Brazilian....	Pernambuco.	1.50	.00079	50–70	Warp	Strong and wiry
	Maranham....	1.15	.00079	50–60	do.	Harsh and wiry
	Ceara.......	1.15	.00079	60	Weft	Good, white, and cohesive staple
	Paraiba......	1.20	.00079	50–60	Warp or weft	Fairly strong, harsh, of good color
	Rio Grande..	1.15	.00079	40–50	Weft	Soft, white, and harsh staple
	Maceio......	1.20	.00084	40–60	Warp or weft	Soft, pliable, and good for hosiery
	Santos.......	1.30	.00084	50–60	Weft	Exotic from American seed, white and silky staple
	Bahia.......	.....	......	40–50	Warp or weft	Fairly strong, but harsh and wiry
American...	Orleans......	1.1	.00077	34–46	do.	Medium length, pearly, white
	Texas.......	1.05	.00077	32–40	do.	Similar to above, rather harsher and more glossy
	Allanseed....	1.20	.00077	50–60	Warp	Good, white, long; blends with brown Egyptian
	Mobile......	1.00	.00076	40–50	Warp or weft	Even-running staple, soft and cohesive
	Norfolks.....	1.00	.00076	40–50	Weft	Used for Oldham counts of 50's
	St. Louis....	0.90	.00076	30–32	Warp	Staple irregular, glossy, but short
	Roanokes....	0.90	.00076	30–34	do.	A white and strong staple
	Boweds......	.....	....	36	Weft	Similar to Uplands
	Benders.....	1.10	.00077	60	Warp	Strong, creamy or white, for Turkey-red dyes
	Memphis....	1.00	00077	40–50	do.	Bluish white, for extra hard twists
	Peelers......	1.25	.00077	60–80	Weft	Long, silky, fine staple; adapted for velvets, etc.
	Uplands.....	1.00	.00077	36–40	do.	Glossy when clean, apt to be dull, sandy, and leafy,
	Alabama.....	0.90	.00077	26–30	Warp or weft	Short staple of less strength, varying color

Types	Variety	L'gth Ins.	Diameter Inches	Counts	Use	Properties
American	Linters			8–10	Weft	Short-stapled gin waste
	Tennessee	0.90	.00077	28	Warp or weft	Of varying length and color
Greek	Smyrna	1.25		36–40	Warp	Harsh and strong, adapted for double yarns
African	Lagos	0.80		20–26	Weft	Dull and oil-stained, irregular in length and strength
West Indian	Carthagena	1.50		26	Warp	From exotic seeds; fairly strong
	La Guayran	1.20		40	Warp or weft	Irregular and short, but silky staple
China	China	1.00		30	Weft	Harsh, short, and white
Australian	Queensland	1.75	.00066	120–200	Warp or weft	Long, white, silky, fine diameter
East Indian	Oomrawuttee	1.00	.00083	26–32	Warp	Short, strong, and white
	Hingunghat	1.00	.00083	28–36	Weft	Best white Indian staple
	Comptah	1.05			Warp or weft	Generally dull and charged with leaf
	Broach	0.90		28–36	Weft	Like Hingunghat, gives good white weft
	Dharwar	1.00		28	Warp	Exotic from American seeds
	Assam	0.50		15–20	Warp	White, but harsh, to blend with other cottons
	Bengals	0.80		20–30	Warp or weft	Dull and generally charged with leaf
	Bilatu	0.50		10–20	do.	Weak, brittle, and coarse
	Dhollerah	0.70		15–20	do.	Strong, dull, and cohesive
	Surat	0.60		10–15	do.	Dull and leafy, often stained
	Scinde	0.50		to 10	do.	Very strong, dull, short, and poor staple
	Tinnevelly	0.80		24–30	do.	Lustrous, white, soft, and adapted for hosiery
	Bhownuggar	1.00		28-30	Warp	White when clean; often leafy and dirty
East Indian	Cocoanada	0.70		10–14	Brown weft	Brown and dull; use as quasi-Egyptian
	Bourbon	1.00		30	Weft	Exotic; of good staple; scarce
	Khandeish	0.80	.00083	20–26	Warp or weft	Similar in class to Bengal
	Madras or Western	0.70		15–20	do.	Used for low yarns in coarse toweling, etc.
	Rangoon	0.60		to 10	Warp or weft	Weak, dull, often stained and leafy
	Kurrachee	0.90		28	do.	Fairly strong, dull and leafy
Italian	Calabria	0.90		26–28	do.	Fairly strong, irregular and dull, leafy
Turkey	Levant	1.25	.00077	36–40	Warp	Harsh, strong, and white

The extreme variation in the length and diameter of different kinds of cotton, according to Bowman,[1] is as follows:

---

[1] "Structure of the Cotton Fiber."

Cotton	Variation in Length	Variation in Diameter
American (Orleans)	0.28 in.	0.000390 in.
Sea-Island	0.39 in.	0.000360 in.
Brazilian	0.28 in.	0.000340 in.
Egyptian	0.22 in.	0.000130 in.
Indian (Surat)	0.25 in.	0.000391 in.

Bowman has found that Egyptian cotton is the most regular both in length and in diameter of filament, while Sea-Island cotton, although possessing the greatest length and fineness of staple, also exhibits the maximum in variation. He has also observed that the variation in diameter is proportionately much larger than the variation in length. He has computed that if a single filament of American cotton be magnified until its diameter reaches one inch, the length will be slightly over one hundred feet, while a similar fiber of Sea-Island cotton of identical diameter would extend about one hundred twenty feet. It requires from 14,000 to 20,000 individual fibers of American cotton to weigh one grain, this being equivalent to about 140,000,000 per avoirdupois pound, the individual fiber having an average weight of only about one six hundred thousandth of a grain. If the separate fibers contained in one pound of such a cotton were placed end to end in a straight line they would extend some 2,200 miles.

The length of staple of the more readily occurring varieties of cotton, according to Höhnel, is as follows:

Gossypium barbadense	(Sea-Island)	4.05 cm.
Gossypium barbadense	(Brazilian)	4.00 cm.
Gossypium barbadense	(Egyptian)	3.89 cm.
Gossypium vitifolium	(Pernambuco)	3.59 cm.
Gossypium conglomeratum	(Martinique)	3.51 cm.
Gossypium acuminatum	(Indian)	2.84 cm.
Gossypium arboreum	(Indian)	2.50 cm.
Gossypium herbaceum	(Macedonian)	1.82 cm.
Gossypium herbaceum	(Bengal)	1.03 cm.

The length and diameter of individual cotton filaments, as shown by mean determinations of Deschamps, Leigh, Alcan, Kuhn, Monie and Bowman, as arranged by C. Mitchell and R. Prideaux, are given in the following two tables:

TABLE XXXVIII.—DIAMETER OF FIBERS

In Micromillimeters (μ) and Fractions of an Inch (1 μ = 0.000039 inch)

	Déschamps		Alcan		Monie	
	μ (Micro-millimeters)	In.	μ	In.	μ	Mean In.
Sea-Island	16.5	0.00064	6.6–13.3	0.00025–0.00052	3.5	0.000635
Fiji	17.2	0.00067	...	...	16.3	0.000637
Egyptian	19.4	0.00076	...	...	17.3	0.000675
Algerian	...	...	10–25	0.00039–0.00097	...	...
U. S. A.	21.0	0.00062	10–22.2	0.00039–0.00057	...	...
U. S. A.:						
Bourbon	22.2	0.00087	...	...	...	...
Orleans	...	...	...	...	19.3	0.000757
West Indian	...	...	...	...	19.7	0.000769
Brazilian:						
Pernambuco	28.0	0.00109	...	...	20.1	0.000787
Maranham	...	...	...	...	20.1	0.000787
Peruvian	21.5	0.00084	13.3–20	0.00025–0.00078	20.0	0.000781
Indian:						
Hingunghat	...	...	...	0.00039–0.00129	21.3	0.000833
Dhollerah	...	...	10–33.3	...	21.7	0.000847
Broach	22.5	0.00088	...	0.00055–0.00118	21.3	0.000833
Comptah	...	...	14.2–30.3	...	21.7	0.000847
Bengal	25.3	0.00098	...	...	22.1	0.000869
W. Madras	22.5	0.00088	11.1–16.6	0.00043–0.00065	21.3	0.000833
N. Madras	20.0	0.00078	11.1–16.6	0.00043–0.00065	...	...
Scinde	...	...	13.3–25	0.00025–0.00097	21.0	0.000819
African	...	...	...	...	19.7	0.000769
Smyrna	26.2	0.00122	...	...	...	...
Chinese	...	...	25–27	0.00097–0.00105	...	...

Moisture in Cotton. The normal hygroscopicity of cotton is less than either that of wool or silk. Under favorable conditions it varies between 5% and 8%, although in an unusually moist atmosphere this amount may be materially increased.

According to Kuhn[1] a portion of this moisture must be regarded as a constituent of the cotton filament, that is "water of constitution." He states the amount is usually about 2% which can be expelled at 105° C. and above, when the fiber then becomes harsh and brittle and loses substantially all its elasticity. The observations of Kuhn, however, have not been corroborated by other investigators.

According to F. Beltzer,[2] Indian cottons under preferable

---

[1] Die Baumwolle page 131. According to J. Huebner and W. Pope (J. S. C. I. 1904, **23**, 404; abst. Zts. Farben. u. Textil. Chem. **2**, 315. Chem. Centr. 1904, **75**, I, 1625; Chem. Zts. 1903–1904, **3**, 77; Jahr. Chem. 1904, **57**, 1813; Zts. ang. Chem. 1904, **17**, 777, the article being illustrated with microphotographs), treatment in boiling water appears to increase the affinity of cotton for substantive dyestuffs, and to decrease it for basic dyestuffs.

[2] Les Matieres Cellulosiques.

TABLE XXXIX.—LENGTH OF COTTON STAPLES.

Description of Cotton	Déschamps		E. Leigh		Alcan		Kuhn		Monie		Bowman	
	Mm.	In.	Mm.	In.	Mm.	In.	Mm.	In.	Mm.	In.	Mm.	In.
Sea-Island, Edisto	58	2.28	48.2–58.4	1.9–2.3			54.5	2.14	31.75–51	1.25–2.0	56	2.20
Fiji	51.25	2.01	47.75	1.88			46.45	1.83	36–57	1.37–2.2	49	1.95
Egyptian	31.75	1.25	31.7–40.6	1.2–1.6			34.30	1.3	31.75–40.7	1.25–1.62	31.7–38	1.25–1.50
Algiers	20 to 35	0.78–1.37	35–40.6	1.3–1.6								
U. S. A. (Upland),												
Georgia	23.50	0.92	31.7	1.20	35–40	1.37–1.57	26.30	1.04	21–26.6	0.81–1.06	26	1.0
(Orleans) Mississippi	26.25	1.03	27.9	1.10			26.70	1.06	23.6–28.4	0.93–1.12		
Louisiana			27.9	1.10	21–26	0.82–1.02	26.30	1.04				
W. Indian											34.3	1.30
Brazilian:												
Pernambuco			23–38	0.9–1.50			31.50	1.19	28.4–40	1.12–1.37	35	1.35
Maranham			31.7	1.20			29.85	1.17	23.6–30	0.93–1.18	29.2	1.15
Paraiba			31.7	1.20			29	1.13			31.7	1.20
Peruvian	28.75	1.13	35	1.30	22–30	0.86–1.18			28.4–36.3	1.12–1.43	34.3–35.2	1.30–1.38
Indian:												
Hingunghat									22.6–30	0.87–1.18	31.7	1.20
Dhollerah	22.75	0.89	27.9	1.10	27.50	1.06–1.96	24.85	0.98	20.5–26.7	0.81–1.06	27.9	1.10
Comptah			26.6	1.05	18–20	0.71–0.78	24.0	0.94	19–26	0.75–1.0	26.5	1.05
Broach	20	0.78	23	0.9			21.4	0.83	17.2–26	0.68–1.0	23	0.90
Berar	20	0.78	23	0.9			23	0.90				
Madras	21	0.82	22	0.85	18–23	0.71–0.90	21.4	0.83	19–26	0.75–1.0	26	1.0
Scinde					16–18	0.63–0.86			13–22.6	0.5–0.87	26	1.0
African:												
Natal			31.7	1.20					22.6–30	0.87–1.18	23.1–40.7	0.91–1.25
Lagos			23	0.90								
Smyrna	23	0.9							22.6–28.4	0.87–1.12	41.9	1.65
Australian			35–47	1.30–1.80								
Chinese	22	0.86			21–25	0.82–0.98						

atmospheric conditions, absorb about 1.5% more moisture than American cottons, although this difference is manifested only within well-defined limits as to the saturation of the air with aqueous vapor. When the relative humidity is 40%–60% the difference in the amount of moisture absorbed is only one per cent. Egyptian cotton is claimed to occupy a position intermediate between the Indian and American cottons in this respect. Beltzer has not corroborated these assertions by experimental proof. The hygroscopicity of cotton as well as other vegetable fibers is of extreme moment in its proper conditioning during the various processes of spinning, carding and finishing to which it is necessarily subjected in the textile arts. This also has an influence on the commercial valuation of the raw material, as the hygroscopical moisture varies proportionately with increase of water vapor in the atmosphere and it, therefore, is necessary to establish a normal standard of reference. The amount of "regain" allowed in the condition of cotton on the European continent is 8.5%. Hartshorne has computed the following table as to the regain of cotton for various temperatures and humidities:

TABLE XL.—REGAIN FOR COTTON AT VARIOUS TEMPERATURES AND PERCENTAGES OF HUMIDITY.

Percentage Humidity	Degrees Fahrenheit					
	50	60	70	80	90	100
40	5.90	5.79	5.65	5.47	5.25	5.05
50	6.89	6.78	6.63	6.45	6.18	5.86
60	8.00	7.87	7.69	7.44	7.13	6.80
70	9.14	9.00	8.79	8.58	8.32	8.05
80	10.58	10.42	10.23	9.95	9.70	9.60
90	12.28	12.10	11.85	11.56	11.43	11.85
100	14.12	14.00	13.80	13.65	13.70	14.50

In determining the influence of moisture on the strength of cotton and cotton fabrics, the Societe Industrielle de Mulhouse[1]

---

[1] A. Scheurer, Bull. Soc. Ind. Mulhouse, 1902, **72**, 34; abst. J. S. C. I. 1902, **21**, 701; Wag. Jahr. 1902, **48**, II, 562. The absorption property of filter paper appears to be due, not so much to the absorption by the capillary tubes of the filaments themselves, as to the capillary interstices formed by the arrangement of the fibers in proximity or juxtaposition to each other (Papierfabr. 1906, **4**, 1834).

have established the following as the normal standards:

Normal strength of cloth	100
Saturated with moisture	104
Dried on hot cylinder	86
Again dampened	103

It would appear from these results therefore, that the alternate moistening and hot drying of cotton induces little or no deterioration. Combination of cotton with water may occur in two distinct forms:

1. As hygroscopic moisture, and
2. As water of hydration.

The hygroscopic moisture is considered as that absorbed from normally moist air and varies in quantity from 8% to 12% depending upon the temperature and vapor tension of the air. This water is completely eliminated by heating the cotton to 105°, the latter then being termed in the trade "desiccated." The water of hydration or water of constitution is separable only at a higher temperature—from 150° to 170° has been required. At these temperatures an additional loss of weight of from 1% to 3% results. The water of hydration may also be estimated by first desiccating the cellulose at 105°, then boiling in toluene and distilling as first pointed out by C. Schwalbe.[1] Cotton containing water of hydration has been called cellulose hydrate or hydrocellulose (see p. 127). The limit of the hydration in cotton may be considered as corresponding to mercerized cotton (see Cellulose Hydrate, p. 213).

It should be noted, however, that the above statements require experimental verification in many instances before final acceptation. Schwalbe determines the hygroscopic water in cotton or other cellulosic fiber as follows: Approximately 3 grams of the material is boiled in 300–500 cc. of pure toluene, which has a boiling point of about 110°. The water is collected by distillation in a graduated tube and from a determination of its volume the percentage of moisture may be calculated, the distillate consisting of two layers of which the water forms the lower. This method is applicable not only to the determination of moisture in normal cellulose but in mercerized cotton and hydrated cellu-

---

[1] Zts. ang. Chem. 1908, **21**, 401, 1321; abst. J. S. C. I. 1908, **27**, 295; Chem. Zentr. 1908, **79**, I, 1336; II, 447; J. C. S. 1908, **94**, ii, 627; C. A. 1908, **2**, 1885, 2448.

lose as well. The following results indicate the amount of moisture as determined by Schwalbe in this manner with varying materials:

Paper made from cotton	6.5 %
Mercerized cotton	9.25%
Mercerized wood pulp	10.25%
Viscose	11.25%
Vegetable silk	6.7 %

Cotton which has been deprived of its hygroscopic moisture by drying in an oven at 100° to 105° by the usual method, rapidly recovers its original amount of moisture after exposure to the atmosphere at room temperature for 10 to 12 hours. When moisture has been removed, however, by means of boiling toluene, the recovery in percentage of water is much less. When the drying operation is conducted at an abnormally high temperature the recovery of moisture is considerably less, so that the normal recovery may be taken as the exact measure of the hygroscopic moisture after the elimination of the water of hydration.

A. Schweizer[1] contends that the estimation of the percentage of moisture in cotton gives only relative figures since the drying is not carried out in an absolutely anhydrous atmosphere but in a more or less moist atmosphere at 105° to 110°. Cotton dried to constant weight at 110° still loses water when dried at 150°, which is taken up again if the temperature is dropped to 110°. If a sample of cotton is conditioned on a damp day and again on a dry day, appreciable different results are obtained, which, in the purchase of large quantities may lead to litigation. Proper significance has not hitherto been attached to these conditions. This author appears in his deductions to have left out of consideration an important factor, viz., the element of time.

Schulz has shown that certain carbohydrates when heated even to 100° become permanently changed, and the same holds good for the cotton fiber if the heating be sufficiently prolonged. Furthermore, J. Lester, contradictory to Schweizer, has shown that when cotton is dried at 110° it never regains the whole of the amount of moisture lost in drying. Lester[2] has found that by

---

1. Leipz. Monatsch f. Text. Ind. 1908, 139; abst. J. Soc. Dyers Col. 1908, **24,** 268; Chem. Ztg. Rep. 1908, **32,** 436.

2. J. S. C. I. 1902, **21,** 388; 1905, **24,** 171; abst. J. Soc. Dyers Col. 1902, **18,** 187; Jahr. Chem. 1902, **55,** 1051; Meyer Jahr. Chem. 1905, **15,** 511; Zts. ang. Chem. 1905, **18,** 1988; Chem. Centr. 1905, **76,** II, 83; Wollen und Leinenind, 1905, **25,** 646.

extracting pure cotton with boiling distilled water, there was frequently obtained as much as 2% of soluble matter and never less than 1.5%. The nature of this "water extract" is very complicated and has, as yet, not been determined, but it is, however, exceedingly hygroscopic, absorbing as much as 28% of moisture. The power of cotton for the absorption of moisture from the atmosphere appears to depend largely upon the presence of this substance. It is apparent that the author's statements evidently refer to raw cotton.

Will[1] has determined the hygroscopicity of a large number of celluloses, by drying the material to constant weight at 40° and exposing it subsequently to an atmosphere saturated with aqueous vapor. His figures for hygroscopicity give the increase of moisture content compared with by the material at 40° in the drying oven to that at 25° in water vapor saturated air.

(A) Natural Cottons:	
Texas wool	7.3%
Sea-Island	7.3%
Superfine machine ginned Seinde	7.4%
Mid fair Georgia	7.9%
Fine Churka Belati	7.3%
East Indian wool, not further designated	8.0%
(B) Other Celluloses:	
Cotton from spinning waste	7.5%
Cleaned cotton rags	6.4%
Swedish woodpulp	7.0%
Woodpulp from Waldhof	6.7%
Hemp	7.7%
Jute	10.8%

The determinations by the same author concerning the influence of purifying the cellulose on the hygroscopicity are as follows:

---

[1] Mitteilungen, **4**, 12. Anon., Pap. Fabr. 1919, **17**, 1919; abst. C. A. 1920, **14**, 469. A. Berglind, Can. P. 192666, 1919; abst. C. A. 1919, **13**, 2762. E. Cadoret and A. Jost, E. P. 8558, 1894. E. Carstensen de Segundo, E. P. 114435, 114450, 1918. N. Fleming and A. Thaysen, Biochem. J. 1920, **14**, 25; abst. J. S. C. I. 1920, **39**, 263-A. C. Henry, E. P. 20092, 1899. M. Mayer, D. R. P. 312178, 1918; abst. J. S. C. I. 1919, **38**, 756-A. T. Moreul, Bull. sci. Pharmacolog. **20**, 101. T. Ogle, U. S. P. 1312348, 1919; E. P. 116214, 1917; abst. J. S. C. I. 1918, **37**, 461-A; 1919, **38**, 678-A. R. Kadish and T. Buscher, U. S. P. 1327394, 1920; abst. C. A. 1920, **14**, 849. O. Kress, Paper, 1920, **25**, 964, 1009; abst. J. S. C. I. 1920, **39**, 858-A. See also J. S. C. I. 1919, **38**, 263-A. F. Stockton, U. S. P. 1295078, 1919; E. P. 132422, 1918; abst. J. S. C. I. 1919, **38**, 319-A, 814-A. A. Streiff, Swiss P. 62103, 1913; abst. C. A. 1914, **8**, 2262. A. Deiss and C. Fournier, D. R. P. Anm. D-22139, 1909; F. P. 403518, 1909.

Manner of Treatment	Hygroscopicity of Cottons			
	Texas Wool	Dynamite Cotton	Sea-Island	Georgia
Initial material	7.3	7.5	7.3	7.9
Pulped	9.8	8.4	9.4	9.3
Extracted with ether	9.7	8.5	9.4	11.2
Treated cold with 2% HCl	5.5	5.4	6.6	5.9
Treated with 5% H_2SO_4	6.5	6.5	6.6	6.3
Boiled with NaOH 10%	6.6	6.6	...	...
Bleached with $CaOCl_2$ 10%	6.3	7.5	...	...
Boiled with H_2O for 50 hours	7.8	6.3	...	...
Dried at 70°	7.0	7.5	...	...
Dried at 100°	6.8	7.2	...	...
Dried at 170°	6.7	7.2	...	...
Dried at 200°	6.1	5.04	...	...

C. Beadle and O. Dahl[1] have determined the gain in weight and also the rise in temperature when the following anhydrous celluloses are exposed to the air: (1) Cotton wool. (2) Cotton wool mechanically pulverized so as to reduce the fibers to about one-twentieth of their former length. (3) Coarsely ground viscoid (an amorphous cellulose). (4) Finely ground viscoid.

(1) and (2) take about 60 minutes to come to constant weight. (1) gains considerably less than (2). The two viscoid samples took nearly four hours to come to a constant weight, but the finely powdered gained considerably less than the coarse. The curves given for the increase in weight show that there is increased regularity with the increased subdivision of the cellulose. The results also show that this holds good whether the cellulose is in the fibrous or amorphous condition.

The temperature curves in which the temperature of the air is reduced to a straight line, show that cotton reaches a maximum of about 4.5° F. in 10 minutes. The temperature gradually falls, and reaches the atmospheric temperature in about 60 minutes. Disintegrated cotton reaches a maximum of 7° F. in 20 minutes, and takes much longer to fall. The curve is also much more regular than that of cotton wool. Both kinds of viscoid fall sud-

---

[1] Chem. News, 1896, **73**, 180; abst. J. S. C. I. 1896, **15**, 352; Bull. Soc. Chim. 1896, **46**, 1851; Chem. Centr. 1896, **67**, I, 1227; Jahr. Chem. 1896, **49**, 1029.

denly below the atmospheric temperature during the first minute. They reach the atmospheric temperature again in about two minutes. They reach a maximum of 7° F., and fall slowly but somewhat irregularly. It appears that each cellulose has a characteristic temperature curve. In each case the degree of fineness affects the regularity of the curves.

It would appear from the investigation of Sindall[1] that the hygroscopic moisture content of completely pulped cellulose is greater than that of ordinary fibrous cellulose, also ground in the pulper. Air-dry sheets of paper gave the following values:

Duration of Pulping	Hygroscopicity
4 hours	5.8%
10 hours	5.9%
17 hours	6.9%
25 hours	6.8%
33 hours	7.0%
After complete drying and exposure to the air for 3 days:	
4 hours	5.18%
10 hours	5.55%
17 hours	6.02%
25 hours	6.00%
33 hours	6.11%
After complete saturation with moisture:	
4 hours	11.2%
10 hours	11.7%
17 hours	12.9%
25 hours	12.5%
33 hours	14.0%

O. Masson[2] has investigated the wetting of cotton by water and by water vapor, and has found that when dried cotton is immersed in water, its temperature rises for some time, and afterwards slowly falls. The same phenomenon occurs when the cotton-wool is exposed to air saturated with aqueous vapor; and in both cases the courses of the curve representing the rise and fall are similar, and are similarly affected by previous moisture and other conditions. In the latter case the effect is due to the condensation on the cotton of vapor which it absorbs, for both absorption and heat-production occur for many hours, and the amount of heat is approximately that calculated from the quantity of vapor absorbed. In the former case, though absorption cannot be directly observed, it must occur, and the air adhering to the

[1] Mon. papet. franc. 1909, **45**, 31.

[2] Proc. Roy. Soc. 1904, **74**, 230; abst. J. S. C. I. 1904, **23**, 1143; Chem. Centr. 1905, **76**, I, 27.

fiber maintains the separation necessary for distillation to occur.

Medical or "absorbent" cotton-wool, though it behaves like ordinary cotton-wool in saturated air, does not show the same rise of temperature in water. The water condensed on the cotton certainly does not combine chemically with it; and it is not simply condensed as a film on the surface, for the quantity is too great for the recognized maximum thickness of such film. It probably undergoes osmotic diffusion into the fiber and forms a sort of solid solution of cellulose and water, having a vapor pressure always lower than that of water. Cotton in air saturated with alcohol vapor, or guncotton or glass wool in air saturated with water vapor, showed similar behavior, though to a slighter extent, and no effect was produced when cotton was immersed in absolute alcohol or glass wool in water, so that the air-insulation is necessary to produce the effect. This thermal effect is much greater than, and probably quite different from that investigated by Parks, occurring when finely divided solids are mixed with water; but the effects long ago observed by Pouillet when finely divided solids were placed in water were probably in part at least, due to distillation.

O. Masson and E. Richards[1] have also determined the amount of moisture which is absorbed by cotton when exposed to an atmosphere of known humidity. "Absorbent" cotton was employed, which, after being washed with distilled water and dried, was wound around the bulb of a thermometer and brought to a constant weight by exposing it for 24 hours in a desiccator containing phosphorus pentoxide. It was then transferred to a porous pot suspended in sulfuric acid of known strength (and hence of known vapor pressure), by which means the interior of the pot was kept constant as to humidity by evaporation from its walls. It is not sufficient to expose the dry cotton to the atmosphere of a given humidity until an apparently constant weight results, because the rate of absorption—which rapidly diminishes—becomes almost inappreciable before absorption is complete. The amount of hygroscopic moisture required by a given weight of cotton to put it in true equilibrium with an atmosphere

---

[1] Proc. Roy. Soc. 1906, **78**, A, 412; abst. J. S. C. I. 1907, **26**, 89; Chem. Zentr. 1907, **78**, I, 594; Meyer Jahr. Chem. 1906, **16**, 28. He considers that the liquids are absorbed by the solids, passing into the solid state themselves. See Martine, Phil. Mag. **47**, 329; **50**, 618.

of given humidity, below the saturation value, is therefore ascertained by taking the mean of the apparent equilibrium values reached by absorption (cotton initially dry) and evaporation (cotton initially over-moist). The progress of either change may be followed by observing the characteristic temperature curve given by the thermometer.

The results obtained are expressed in the following table, which shows the amount of moisture absorbed by 0.948 gm. (W) of pure cotton over sulfuric acid solution at 20°; "p" is the actual pressure of water vapor in the atmosphere employed; "P" is the saturation pressure of water vapor at the same temperature; "Ma" is the weight of water absorbed by the sample of dry cotton of weight W, after exposure in the apparatus until further absorption appears negligible. "Me" is the weight of water retained by the same sample after it has been supersaturated by exposure over water and then allowed to evaporate in the apparatus until further loss appears negligible, and "M" is the arithmetic mean of Ma and Me, and is taken as indicating the amount of absorbed moisture which is required to establish true equilibrium.

Acid Employed			Ma	Me	M	M/W
Sp. gr. 20° C.	H_2SO_4 %	p/P				
1.6516	73.8	0.050	0.0120	0.0145	0.0132	0.0139
1.5724	67.0	0.100	0.0175	0.0198	0.0186	0.0196
1.4850	59.0	0.198	0.0264	0.0311	0.0288	0.0304
1.4167	52.6	0.294	0.0356	0.0406	0.0381	0.0402
1.3672	47.2	0.408	0.0441	0.0497	0.0469	0.0495
1.3282	43.1	0.500	0.0509	0.0593	0.0551	0.0581
1.3028	40.5	0.556	0.0530	0.0655	0.0592	0.0624
1.2887	38.8	0.598	0.0599	0.0690	0.0644	0.0679
1.2368	32.3	0.710	0.0716	0.0840	0.0778	0.0821
1.1930	26.8	0.794	0.0860	0.1002	0.0931	0.0982
1.1616	23.2	0.844	0.0989	0.1107	0.1048	0.1106
1.1398	20.3	0.874	0.1045	0.1250	0.1148	0.1210
1.1226	18.1	0.894	0.1114	0.1300	0.1207	0.1274
1.0686	10.3	0.952	0.1378	0.1606	0.1492	0.1574
1.0378	6.2	0.972	0.1563	0.1792	0.1678	0.1770

By multiplying the last columns by 100, the percentage absorption is shown.

Cotton containing a definite proportion of moisture resembles an aqueous solution in that it exercises a vapor tension which is, at different temperatures, a constant fraction of that of pure water. Different weights of the same cotton have the same vapor tension when they contain the same percentage weights of hygroscopic moisture, and the results are not influenced by tight or loose packing. Filter paper gives results very similar to those obtained with cotton-wool. It is also shown that, by observing the rate of rise of temperature of dry cotton when first exposed to moist air, the pressure of aqueous vapor in the atmosphere may be determined, thus providing a new method of hygrometry.

L. Vignon[1] has determined the specific gravity of cellulose when wetted with benzine, selecting this fluid because it wets the fiber well, and also permits the elimination of adhering air and other gases by vacuum exhaustion. Using an ordinary hydrostatic balance, at 18°, and cotton of normal atmospheric moisture, he found absorbent cotton to have a sp. gr. 1.50 and ordinary cotton yarn, 1.51. In measuring the absorptive power of cotton for water at ordinary temperatures, Vignon[2] obtained independently from the weight of the fiber, an absorption of 495, calculated on 100 gm. According to C. Beadle[3] cotton takes up 100% in the cold, and 63% when warm, the moisture being taken up through the cell-wall.

Cellulose undergoes peculiar changes through freezing and the subsequent expansion by the solidification of the intersticial water. The aqueous crystals forming in the intercellular lumen cause a loosening and breaking of the fiber or fiber bundles. It is the opinion of Erfurt[4] that the freezing of half-finished paper pulp materially changes the paper-forming qualities of the stock. Such frozen pulp is especially suitable for the manufacture of filter paper, and in fact, the so-called Swedish filter paper, gen-

---

[1] Compt. rend. 1892, **114**, 424; abst. J. S. C. I. 1892, **11**, 1002; Chem. Centr. 1892, **63**, I, 616; Jahr. Chem. 1892, **45**, 2906; Chem. Tech. Rep. 1892, **31**, I, 103; Ber. 1892, **25**, 268; Bull. Soc. Chim. 1892, **7**, 247; Mon. Sci. 1892, **39**, 309; Rev. gén. sci. 1892, **3**, 170; Deut. Chem. Ztg. 1892, 92.

[2] Compt. rend. 1898, **127**, 73; abst. J. S. C. I. 1898, **17**, 841; Bull. Soc. Chim. 1898, **19**, 919; Mon. Sci. 1898, **51**, 607; Chem. Centr. 1898, **69**, II, 455; Jahr. Chem. 1898, **51**, 834.

[3] Chem. News, 1897, **75**, 74; 1902, **86**, 88; Chem. Centr. 1897, **68**, I, 571, 573; Jahr. Chem. 1897, **50**, 485, 1506. D. R. P. 70999; abst. Mon. Sci. 1893, **42**, 304; 1897, **50**, 128; 1905, **63**, 325; Ber. 1893, **26**, 999; Chem. Centr. 1894, **65**, I, 365; Wag. Jahr. 1893, **39**, 1001.

[4] Papierfabr. 1907, **1**, 1687.

erally conceded as one of the best, owes its desirable qualities to such a treatment.

It is the judgment of C. Rothwell[1] that the individual cellulose filaments do not lose in strength through repeated freezing and thawing. Boiling water has but little effect upon cotton cellulose. H. Tauss[2] found that Swedish filter paper on being boiled with water for three hours under ordinary pressure with distilled water, gave off traces of an extract, which reduced Fehling's solution. Boiling water also induces a small but evident plasticity in cellulose, which, however, is permanent. Boiling in water, however, does not appreciably affect the hygroscopicity.

In printing, changes in cellulose have been observed when the fiber has been treated with steam. It is possible to thus fix diamine and other substantive colors on cotton fiber by wet steaming, especially when glycerol is present.[3] J. Mueller[4] considers this process a transformation of the fiber in the state of gel, i. e., indicating the colloidal properties of the fiber.

Cellulose is partly dissolved by boiling with water under pressure. H. Tauss found the following results for Swedish filter paper: 20 gm. cellulose in 1 liter water heated for 3 hours under a pressure of 5 atmospheres:

Drying Residue of the Aqueous Extracts:	1	2	3	Total
For 20 gm.	0.148	0.088	0.049	0.277 gm.
For 100 gm.	0.740	0.400	0.245	1.385 gm.

The boiling was repeated successively for three times with the same material. The decrease of the soluble matter in each boiling becomes very apparent. The liquids were evaporated, dried carefully at 100° for 3 hours and weighed. A blue to bluish violet sugar-like substance was determined with Fehling's solution and calculated as dextrose:

Sugars Found:	1	2	3	Total
For 20 gm.	0.021	0.0025	0.0012	0.0247 gm.
For 100 gm.	0.105	0.0125	0.0060	0.1235 gm.

---

[1] Faerb. Ztg. 1892–1893, 75; J. S. C. I. 1892, **11**, 320; abst. Chem. Ztg. 1892, **16**, 191; Jahr. Chem. 1892, **45**, 2906; Wag. Jahr. 1892, **38**, II, 962.

[2] Dingl. Poly. 1889, **273**, 276; Chem. News, 1890, **61**, 169; J. S. C. I. 1889, **8**, 913; Mon. Sci. 1890, **35**, 164; Ber. 1889, **22**, R, 769; Chem. Centr. 1889, **60**, II, 444; Chem. Ind. 1889, **12**, 514; Chem. Tech. Rep. 1890, **39**, II, 105; Jahr. Chem. 1889, **42**, 2838; Wag. Jahr. 1889, **35**, 1; Apotheker Ztg. 1890, 232; Chem. Ztg. 1890, **14**, 232.

[3] Zts. Farb. Ind. 1904, **3**, 390; Faerb. Ztg. 1905, **16**, 138.

[4] Bull. soc. ind. Rouen, 1904, 390.

According to the statement of Mulder,[1] a little glucose results when cellulose is boiled with water at 200°. F. Hoppe-Seyler[2] observed that when filter paper is heated for 4–5 hours in sealed tubes at 200°, carbon dioxide is given off, while formic, acetic and protocatechuic acids and pyrocatechol are formed. However, when the experiments were conducted in a neutral (platinum) receptacle,[3] no protocatechuic acid or pyrocatechol is formed, thus proving that alkali is required for its formation from cellulose. C. Williams[4] found furfurol in the liquid from heating cellulose with water under pressure.

Nitrogen in Cotton. R. Haller[5] has shown that cotton at any stage of its manufacture is dyed slightly by an acidulated solution of safranine, the shades obtained being fast to washing. He ascribed this property to the cutinized outer cuticle and to the presence of nitrogenous substances in the inner cuticle and in the dried-up residue of the cell contents. Bleached cotton is less deeply tinted than unbleached. A. Schindler[6] confirms Haller's view by a determination of the nitrogen contents of Egyptian cotton in the raw and partially bleached states. The cotton used was in the form of silver and the nitrogen was estimated by Kjeldahl's process. Two determinations on the raw material gave 0.256% and 0.250% of nitrogen. Two determinations on material which had been boiled for eight hours in caustic soda of 1.01 sp. gr. showed 0.066% and 0.064% nitrogen respectively. Another sample, boiled for eight hours with caustic soda of 0.05 sp. gr. contained only 0.028% of nitrogen. It was found that on boiling in

---

1. J. prakt. Chem. 1844, **32,** 336; abst. Scheik Onderzoek, **2,** 76; Ann. 1841, **39,** 150.

2. Ber. 1871, **4,** 15; abst. Chem. News, 1871, **23,** 131; J. C. S. 1871, **24,** 226; Bull. Soc. Chim. 1871, **15,** 98; J. pharm. chim. 1872, (4), **15,** 414; Jahr. Chem. 1871, **24,** 476.

3. Zts. physiol. Chem. 1889, **13,** 66–121; abst. J. S. C. I. 1889, **8,** 404. See also C. Eggertz, Bied. Centr. 1889, **18,** 75; abst. J. S. C. I. 1889, **8,** 293.

4. Chem. News, 1872, **26,** 231, 293; abst. J. C. S. 1873, **26,** 162; Bull. Soc. Chim. 1873, **19,** 162; Jahr. Chem. 1872, **25,** 760; Amer. Chem. 1872, **3,** 308, 353.

5. Zts. Farben. Ind. 1907, **6,** 125, 127; abst. J. S. C. I. 1907, **26,** 523; Chem. Zentr. 1907, **78,** II, 953; 1908, **79,** II, 113; Chem. Ztg. Rep. 1907, **31,** 257; Jahr. Chem. 1905–1908, II, 3185; Wag. Jahr. 1908, **54,** II, 376; Zts. ang. Chem. 1907, **20,** 2085; 1908, **21,** 267. See also Textile ü. Farben. Ztg. **14,** 221; abst. C. A. 1907, **1,** 2495; Chem. Ztg. 1908, **32,** 838; abst. Meyer Jahr. Chem. 1908, **18,** 505.

6. J. Soc. Dyers Col. 1908, **24,** 106; abst. J. S. C. I. 1908, **27,** 497; Meyer Jahr. Chem. 1908, **18,** 504. Compare Chem. Ztg. Rep. 1908, **32,** 314.

strong caustic soda of 77° Tw., ammonia was evolved corresponding to 0.06% of nitrogen in the cotton taken, and two determinations of thenitrogen remaining in the cotton under this treatment gave 0.019% and 0.016%; thus it appears that upon boiling with caustic soda, the bulk of the nitrogenous matter present in the cotton, goes into solution in the caustic liquor.

E. Knecht and W. Hall[1] have made systematic extractions of 2-ply, 60's American and Egyptian yarns. Both the alcoholic and aqueous extracts were extremely rich in mineral matter, a considerable portion of which consisted of potassium salts. On dialysis of the aqueous extract, it was separated into a diffusible portion extremely hygroscopic, and a residue, which on evaporation yielded a non-hygroscopic, brittle, resinous substance. Nitrogen determinations carried out on the yarn after each treatment, gave results showing that benzene, water and alcohol extracted only 14.1%-16.7% of the total nitrogenous matter. Experiments on the removal of the nitrogenous matter from raw cotton in a single treatment showed that boiling at atmospheric pressure for 6 hours with 2% caustic soda solution removed 78%-80% of the total nitrogen; boiling with lime for 12 hours removed 37.5%, but this amount was increased by subsequent souring to 53.1%; hot soaping removed only 17.5%.

Further experiments in imitation of the industrial process, boiling under 35 lbs. pressure per sq. in. showed with a yarn containing originally 0.248% nitrogen, the following results representing the proportion of N remaining in the yarn after each stage (original = 100): After lime boil, 54%; sour, 40.5%; after caustic boil, 27.1%; after sour, 26.8%; after bleach liquor, 6.7%; after sour, 5.8%.

A preliminary examination made of the various extracts, yielded the following results: The lime extract gave a gelatinous precipitate with alcohol, free from N and corresponding with pectic acid. The alcohol-soluble portion gave two brown resinous substances of different solubilities, containing 9.1% and 9.6% of nitrogen respectively. A small quantity of fatty acid was also isolated. The total substances extracted from the cotton by the lime boil was 2.1%, which included the major portion of the

---

[1] J. Soc. Dyers Col. 1908, **34**, 220; abst. C. A. 1919, **13**, 909; J. S. C. I. 1919, **38**, 7-A.

mineral constituents of the cotton. The first HCl extract (lime sour) comprised mainly a fatty acid apparently corresponding with stearic acid, together with a dark colored wax, m. pt. 77°–80°; there was also a small quantity of a brown resinous substance similar to that present in the lime extract. The portion extracted by caustic soda yielded a brown residue fairly rich in nitrogen and phosphoric acid.

The solid residue yielded a further quantity of alcohol-soluble coloring matter; the alcohol-insoluble portion giving the general reactions of protein. On acidification of the soda extract a dark-colored protein containing 18.75% nitrogen was isolated. From this extract was also obtained a black, brittle shining mass, soluble in ammonia and assaying 9.6% N, together with a mixture of pectic acid and coloring matter. The total amounts of substances extracted from cotton by the three main treatments outlined above was 4%. The hygroscopic moisture of the raw cotton was 7.36%, and that of the scoured and bleached cotton, 6.14%, thus confirming that the moisture content of unbleached yarn is not wholly dependent on the cellulose present, but partly on the normal accompanying hygroscopic substances.

According to S. Higgins[1] it is quite certain that the proteins of cotton fiber are similar to the protein of the seed intelf. It has been shown by other investigators that a boil with strong sodium hydroxide removed a high per cent. of nitrogen from cotton. During extractions with weak alkalis the proteins are probably little changed, and if the alkali is not too strong this can be used as a method of separating proteins. In the present study the method of T. Osborne, C. Leavenworth and C. Brautlecht[2] was used consisting in distilling 1 gram air-dried protein with 300 cc. of tenth-normal sodium hydroxide, titrating the first 200 cc. distillate with $N/10$ sulfuric acid, making up the residual solution to 300 cc. with $N/10$ sodium hydroxide and again distilling, etc. In the experiments, 30 grams of air-dried material were used. Warp threads were used as these represented foreign matter in addition to actual fiber introduced

---

1. J. Soc. Dyers Col. 1919, **35**, 165; abst. C. A. 1919, **13**, 2604.
2. Amer. J. Physiol. 1908, **23**, 179; abst. C. A. 1910, **4**, 2153; J. C. S. 1909, **96**, I, 72; Chem. Zentr. 1909, **80**, I, 385; Jahr. Chem. 1909, **62**, 1479.

during the manufacturing process. The amount of sodium hydroxide used was equivalent to a 4% boil based on the weight of the material.

The results are recorded in four tables: (1) With American yarn, Egyptian yarn, and linen yarn. (2) Results of 1 calculated to nitrogen and compared with nitrogen in two typical proteins from wheat and peas. Using the customary method of multiplying nitrogen by 6.25 for proteins we have Egyptian 0.275 nitrogen or 1.72% protein, which is not the case. The inference is that not all the nitrogen in the sample was present as protein, and it can be said that the elimination of proteins from cotton during bleaching cannot be measured by simple nitrogen determinations as indicated by C. Cross.[1] (3) Shows comparative results of original American yarn, with yarn in various stages of treatment with sodium carbonate, sodium hydroxide, calcium hydroxide, calcium hypochlorite, etc. (4) Same as for linen. It is a noteworthy fact that sodium hydroxide removes the proteins more effectively from linen than from cotton, which is also the case with lime boil, sour or soda ash boil. In the case of soda ash, however, the effect is not the same as with cotton as the proteins are only partly removed from linen.

It is shown that cotton or linen when scoured with sodium hydroxide or treated with lime sour soda ash, is incapable of forming chloramines on treatment with bleaching powder solutions because it no longer contains appreciable quantities of proteins, and it may be concluded that the formation of chloramines is of no interest to bleachers of cotton and linen. With linen an eight-hour boil with soda ash did not remove all protein and commerically boiled yarns contain a large amount of residual protein. When these boiled yarns are brought into contact with bleaching powder solution to produce what is commonly called commercial "cream" yarns one has the only possibility of the existence of chloramines in the bleachers experience. Cotton piece goods contain warp threads sized with flour, and therefore the nitrogen content of the goods is higher than linen piece goods which are not sized with materials having a high nitrogen content. This fact and the results given in this paper are difficult to reconcile

---

[1] J. Soc. Dyers Col. 1918, **34**, 76.

with the statement of C. Cross, E. Bevan and J. Briggs[1] that cotton cellulose is permanently stained by the taking up of products (containing nitrogen) of the action of the alkali upon flax constituents. Moreover their statement that the nitrogenous constituents of fiber are extremely resistant and only gradually broken down by alkali wash is not borne out by his experience.

Mineral Constituents of Cotton. The average ash content of raw cotton as recorded by different investigations vary within comparatively wide limits and may be set down as from 1% to 2%. Whether or not the ash constituents participate materially in the structural formation of the fiber, whether the base is potassium, sodium, calcium, iron and aluminium found in the ash are bound to the organic molecule in some manner, and whether this is or is not the same in the case of silicic acid, are questions which have not as yet been definitely determined. Regarding the latter, the earlier investigations of A. Ladenburg[2] and W. Lange[3] have shown that silicic acid does not play any important part in the building up of the shafts of straw. W. Tottingham investigated the organic silicon compounds in Graminae.[4] It is quite probable that the mineral matters are merely impurities retained by the colloidal cellulose, a view which is partly confirmed, if it is considered that the so-called ashless filters contain only 0.003%–0.05% of ash.[5]

For incandescent mantle manufacture, cotton and ramie cellulose have been produced which contain but 0.015% ash. and absorbent cotton with less than 0.3%.[6] The above named bases are frequently bound to chlorine and sulfuric and phosphoric

---

[1] J. S. C. I. 1908, **27**, 260; abst. C. A. 1909, **3**, 1213; J. C. S. 1908, **94**, i, 374; Chem. Zentr. 1908, **79**, II, 639; Jahr. Chem. 1905–1908, II, 4505; Meyer Jahr. Chem. 1908, **18**, 505; Wag. Jahr. 1908, **54**, II, 473; Zts. ang. Chem. 1908, **21**, 2509.

[2] Ber. 1872, **5**, 568; abst. Jahr. Chem. 1872, **25**, 795; Bull. Soc. Chim. 1872, **18**, 271; Chem. News, 1872, **26**, 36; J. C. S. 1872, **25**, 910.

[3] Ber. 1878, **11**, 822; abst. J. C. S. 1878, **34**, 682; Chem. Centr. 1878, **49**, 458; Jahr. Chem. 1878, **31**, 948; Jahr. rein Chem. 1878, **6**, 48.

[4] Trans. Amer. Chem. Soc. June 6 and July 7, 1908; abst. Science, **28**, 188; abst. Zts. ang. Chem. 1908, **21**, 2419.

[5] G. Bumcke and R. Wolffenstein, Ber. 1899, **32**, 2495; abst. J. S. C. I. 1899, **18**, 940; Jahr. Chem. 1899, **52**, 1290; J. C. S. 1899, **76**, i, 852; Chem. Centr. 1899, **70**, II, 752; Bull. Soc. Chim. 1900, **24**, 620; Meyer Jahr. Chem. 1899, **9**, 300.

[6] C. Böhm, Prom. 1908, **19**, 14. See also Chem. Ztg. **33**, 447; C. A. 1909, **3**, 2218; Chem. Zentr. 1909, **80**, I, 1732; Meyer Jahr. Chem. 1909, **19**, 329, 330; Zts. ang. Chem. 1909, **22**, 1280; J. Gasbel. **52**, 855; Bayer. Ind. 1909, 255; Wag. Jahr. 1909, **55**, I, 102.

acids. Fluorine is but rarely found, but frequently overlooked on account of its volatility. Zinc is also occasionally met with. With the latter, however, it is claimed that it is a regular constituent of the ash from plants. The United States Department of Agriculture in Bulletin No. 23 gives the average composition of the American cotton plant and its parts as follows: Roots, 8.8%; stems, 3.15%; leaves, 20.25%; bolls, 14.21%; seed, 23.5%; lint, 10.56%.

The mineral constituents in a crop of cotton yielding one hundred pounds of lint per acre, expressed in pounds per acre—the weight of the entire crop being 947 pounds— are given as follows:

Part of Plant	Lbs.	Nitrogen	Phosphoric Acid	Potash	Lime	Magnesia
Roots.....	83	0.76	0.43	1.06	0.53	0.34
Stem.....	219	3.20	1.29	3.09	2.12	0.92
Leaves.....	192	6.16	2.28	3.46	8.52	1.67
Bolls.....	135	3.43	1.30	2.44	0.69	0.54
Seed......	218	6.82	2.77	2.55	0.55	1.20
Lint	100	0.34	0.10	0.46	0.19	0.08
Total.....	947	20.71	8.17	13.06	12.60	4.75

The following table indicates the amount of ash contained in different varieties of cotton lint according to Matthews and Monie:

	Matthews	Monie
Dharwar...............................	4.16	....
Dhollerah...............................	6.02	4.10
Sea-Island...............................	1.25	1.10
Peruvian soft...............................	1.68	1.80
Peruvian rough...............................	1.15	1.25
Bengal...............................	3.98	5.30
Broach...............................	3.14	2.58
Oomrawuttee...............................	2.52	2.93
Egypt brown...............................	1.73	1.60
Egypt white...............................	1.19	1.75
Pernambuco...............................	1.60	1.98
American...............................	1.52	Texas 2.1 Orleans 1.6

J. Barnes[1] has reported upon the analyses of five samples of American cotton which gave from 1.18% to 1.92% of ash; two samples of Egyptian cotton gave 1.37%–1.50% respectively; twelve samples of Indian cotton averaged 2.48% ash, the extremes being 1.34% and 3.99%. The amount of silica and chlorine in the ash support the figures for total ash. There was no apparent relation observable between the moisture content of the lint and the amount of ash. The mineral substances which appear in the ash are in the fiber end on the outside. Analysis of the ash of a Bombay sample of lint gave:

Silicon dioxide	15.56%
Aluminum oxide	10.80%
Ferric oxide	5.80%
Calcium oxide	9.75%
Magnesium oxide	1.87%
Potassium oxide	27.32%
Sodium oxide	4.51%
Sulfur dioxide	1.96%
Phosphorus pentoxide	3.26%
Chlorine	6.55%
Carbon dioxide	12.19%
Undetermined	0.34%

A Punjab sample of cotton ash gave:

Silicon dioxide	14.40%
Aluminum oxide	12.87%
Ferric oxide	12.92%
Calcium oxide	10.65%
Magnesium oxide	4.36%
Potassium oxide	26.03%
Sodium oxide	8.40%
Sulfur dioxide	2.52%
Phosphorus pentoxide	4.46%
Chlorine	3.84%
Carbon dioxide	8.03%
Undetermined	2.52%

Analyses have indicated that cotton grown on saline soil does not contain more mineral matter than cotton grown on other soils. There is little doubt but that the high mineral content of cotton affects the action of the fiber to dyes.

Matthews, "Textile Fibers," page 212 gives the following:

---

[1] J. S. C. I. 1916, **35**, 1191; abst. C. A. 1917, **11**, 890; Chem. Zentr. 1917, **88**, I, 832; Ann. Rep. Soc. Chem. Ind. 1917, **2**, 126, 161.

MINERAL CONSTITUENTS OF TRUE COTTON FIBER.

	Ure %	Davis, Dreyfuss and Holland.* %
Potassium carbonate	44.8	33.22
Potassium chloride	9.9	10.21
Potassium sulfate	9.3	13.02
Sodium carbonate	....	3.35
Calcium phosphate	9.0	.....
Calcium carbonate	10.6	20.26
Magnesium phosphate	8.4	8.73
Magnesium carbonate	....	7.81
Ferric oxide	3.0	3.40
Aluminum oxide and loss	5.0	.....

* Mean % 12 different varieties.

Tensile Strength of Cotton. Cotton stands midway between silk and wool in tensile strength, whereas in elasticity and resiliency it is considerably below either of the other two named fibers. The breaking strain of cotton usually varies from 2.5 to 10 grams, depending on the fineness of the staple; the finer the staple, of course, the less will be its breaking strain. The following table indicates the results of experiments on the tensile strength of different varieties of cotton:

Cotton	Mean Breaking Strain	
	Grains	Grams
Sea-island (Edisto)	83.9	5.45
Queensland	147.6	9.59
Egyptian	127.2	7.26
Maranham	107.1	6.96
Bengal	100.6	6.53
Pernambuco	140.2	9.11
New Orleans	147.7	9.61
Upland	104.5	6.79
Surat (Dhollerah)	141.9	9.22
Surat (Comptah)	163.7	10.64

Herzfeld[1] has prepared the following table as showing the strength in grams of single cotton yarns, of different counts, the numbering of the yarns being according to the metric system:

---

[1] "Yarns and Textile Fabrics," page 95.

No.	Weak	Medium	Strong	Very Strong	No.	Weak	Medium	Strong	Very Strong
4	880	1000	1250	......	32	125	170	200	250
6	670	920	1080	1340	34	120	160	190	220
8	500	690	810	1000	36	110	150	180	210
10	400	550	650	800	38	105	140	170	200
12	330	460	540	660	40	100	135	160	190
14	285	390	460	570	50	......	110	130	140
16	250	340	400	500	60	......	90	110	125
18	220	300	360	440	70	......	80	90	105
20	200	280	320	400	80	......	70	80	95
22	180	250	295	360	90	......	60	70	85
24	170	230	270	330	100	......	55	65	80
26	150	210	250	310	110	......	50	60	70
28	140	200	230	290	120	......	45	55	60
30	130	180	215	260	....	......	....	......	......

A. Scheurer[1] has studied the influence of various operations upon the tenacity of cotton tissues, the numbers given below representing the average result obtained in 20 experiments, the breaking strain of the warp threads of the tissue employed (75 × 26 Alsation counts) being determined:

		Relative Tenacity
1.	Bleached tissue (standard)	100
2.	Hung for a month in an ageing room	98
3.	Hung for a month in a drying chamber	96
4.	Hung for a month in a drying chamber for woolen tissues	96
5.	Exposed for a month to air and rain	98
6.	Passed 20 times through a bleach-house washing machine	96
7.	Soaped for six hours at 212° C. (2 gm. of soap per liter)	101
8.	Soaped for 12 hours at 212° C. (2 gm. of soap per liter)	99
9.	Passed 10 times round a calendering roller (= 20 crushes)	80
10.	Treated as 9, followed by a washing	78
11.	Damped and dried on a drying cylinder 20 times in succession	97
12.	Boiled for 30 minutes in a solution of sodium carbonate (10 gm. per liter)	100
13.	Treated with a 5% solution of hypochlorite of lime at "7° Bé.," dried on a drying cylinder, and then treated as 12	100
14.	Treated as 13 twice	98

Two experiments were made with sateen tissue which was passed twenty times through a continuous washing machine with

---

[1] Bull. Soc. Ind. Mulhouse, 1902, **72**, 33; abst. J. S. C. I. 1902, **21**, 702; J. Soc. Dyers Col. 1902, **18**, 188; Wag. Jahr. 1902, **48**, II, 562.

tension. On testing it the tenacity was found to have diminished in one experiment by 88 (warp threads) and 82 (weft threads), and in the other experiments to 86 and 96 respectively, the original tenacity of the tissue being taken as 100.

Absorption of Gases by Cotton. Cotton has an enormous capacity for the absorption of gases, and it is to this property that the greater effect of chlorine upon cotton than upon other bleached fibers, such as flax, is attributable. In the anhydrous condition, cotton fibers are said to be capable of absorbing more than one hundred times their volume of ammonia gas.

Effect of Reagents on Cotton Fiber. It has generally been stated that in mercerized and well-bleached cotton the cuticula is absent, but the observations of W. Minajeff[1] do not support this contention. The cuticula contains as incrustants, fat, wax, coloring matter, and a substance called cutin which is insoluble in sulfuric acid, so that processes in which alkaline agents are used such as boiling and mercerizing, as well as bleaching, will affect it, only so far as these waxy and fatty bodies are concerned. In most cases it is difficult to distinguish cuticula under the microscope, the different mechanical and chemical treatments through which the cotton undergoes from the raw state, preparatory to its acceptability for nitrating increasing the difficulties of distinction.

The author has studied the action of reagents on the cotton fiber under the microscope and arrived at the following conclusions: The cuticula of the raw cotton fiber resists treatment with concentrated cuprammonium solution, fairly strong sulfuric acid (but not the concentrated acid) and concentrated alkaline liquors both during boiling and during mercerizing; the cuticula of the bleached fiber have the same properties as those of the unbleached filament although not so strongly marked; the fiber walls are substantially completely soluble in concentrated cuprammonium solution and swell strongly when treated with more dilute solutions They are dissolved by concentrated sulfuric acid, being changed to a substance of the nature of amyloid, and swell in weaker

---

[1] Zts. Farben. Ind. 1905, **4**, 81; 1907, **6**, 234, 252, 309, 345; 1908, **7**, 1, 17; 1909, **8**, 313; abst. J. S. C. I. 1907, **26**, 1236; Chem. Centr. 1905, **76**, I, 906; 1908, **79**, I, 308, 1652; Chem. Ztg. Rep. 1908, **32**, 220; Jahr. Chem. 1905–1908, II, 3175; Wag. Jahr. 1908, **54**, II, 458; Zts. ang. Chem. 1908, **21**, 1252, 1255.

solutions but show no change under the microscope when left for a long time in a 10% solution of the acid. They are changed during mercerizing in a manner well known. The fiber walls suffer important changes during the process of oxidation (production of oxycellulose); they become weakened and brittle in this state but are not dissolved by cuprammonium solution. The inner protoplasmic covering of the fiber behaves somewhat similar to the cuticula.[1]

Composition of Cotton. Raw cotton contains the following constituents: (a) cellulose; (b) moisture; (c) oily matter, identical with cotton seed oil, and also other fatty substances; (d) a small proportion of a solid wax, resembling ceresin, which is present as a thin protective layer on the outer walls of the cotton fiber; (e) nitrogenous (proteid and amido) bodies consisting mainly of the protoplasmic residue in the lumen with other related products, which substances coat the walls of the central canal; (f) pectins and other gum-like bodies; (g) cutin (cuticular celluloses) and unchanged cell-contents; (h) small quantities of other organic substances as tannic acid, coloring matter, etc., the latter being present only in traces. They are of a resinous non-crystalline nature, and contains 6%-9% of nitrogen;[2] and (i) mineral matter (containing potassium, calcium, sodium, magnesium, aluminium, and iron with carbonates, chlorides, phosphates and sulfates).

According to the U. S. Department of Agriculture[3] the following represents the composition of the cotton fiber: cellulose 83.71; water 6.74; nitrogen-free extract 5.79; ash 1.65; protein 1.50 and fat 0.61. A more detailed analysis is also given of substances (called "fertilizing constituents") present in the cotton fiber; the analyses having been made from representative specimens

---

[1] H. Lange, Färber. Ztg. 1898, **9**, 197, 234; abst. J. S. C. I. 1898, **17**, 839, 917. In this connection see J. Huebner and W. Pope, J. S. C. I. 1904, **23**, 404; Zts. Farben. u. Textil Chem. **2**, 314; Rep. Chim. 1904, **4**, 446; Rev. gén. sci. 1904, **15**, 470; Chem. Centr. 1904, **75**, I, 1625; Chem. Zts. 1903–1904, **3**, 77; Jahr. Chem. 1904, **57**, 1813; Zts. ang. Chem. 1904, **17**, 777.

[2] See E. Schunck, Mem. Manchester Lit. Phil. Soc. 1868, (3), **4**, 95. Refer to topic "Wax in Cotton."

[3] Bulletin 33. As the result of a large number of tests, the U. S. Dept. Agriculture gives the following, as representing the average composition of a large number of cotton fiber analyses: water, 6.74%; ash, 1.65%; protein, 1.50%; cellulose, 83.71%; nitrogen-free extract, 5.70%; fat, 0.61%.

selected so as to insure an average composition from a wide area:

	Per Cent.
Water	6.07
Ash	1.37
Nitrogen	0.34
Phosphoric acid	0.10
Potash	0.46
Soda	0.09
Lime	0.19
Magnesium	0.08
Ferric oxide	0.02
Sulfuric acid	0.60
Chlorine	0.07
Insoluble matter	0.05

According to Mitchell and Prideaux,[1] there is considerable difference in the ash and phosphoric acid content of various cottons. Indian cotton (Bengal) they find to contain 0.15% phosphoric acids and as high a figure as 0.37% in Pernambuco cotton. F. Calvert[2] obtains 0.027% of soluble phosphoric acid in Surat cotton and 0.055% in Egyptian.

The above figures can only be accepted as representative of a particular cotton, as the proportion of the various constituents present in cotton depends to some extent on the nature of the cotton, the conditions under which it grew, the climate, the soil, the extent of ripeness when collected, cultivation and harvesting. F. Bowman[3] gives the following figures as the average composition of various types of cotton fiber selected during three seasons:

	Surat	American	Egyptian
Cellulose	91.35	91.00	90.80
Wax, oil, and fat	0.40	0.35	0.42
Protoplasm and derivatives (pectoses)	0.53	0.53	0.68
Mineral matter	0.22	0.12	0.25
Water	7.50	8.00	7.85

The cotton as received for nitration often contains impurities introduced during the treatments which the raw material has

---

[1] "Fibers Used in Textile Industries," p. 96.

[2] J. Chem. Soc. 1867, **20**, 303; Compt. rend. 1867, **65**, 1150; J. prakt. Chem. 1867, **101**, 441; 1869, **107**, 122; Chem. News, 1869, **20**, 121; Jahr Chem. 1869, **22**, 800; 1870, **23**, 1150; Chem. Centr. 1867, **12**, 831; Bull. Soc. Chim. 1868, **10**, 174; Zts. Chem. 1867, 539. His figures are: Maceo cotton, 0.05% phosphoric acid; Carthegena, 0.035%; Bengal, 0.055%; Cyprus, 0.05%; Egyptian, 0.055%; New Orleans, 0.049%. Analysis of the cotton seeds gave in phosphates, results as follows: Magnesium phosphate, 0.652; iron phosphate, 0.053%; alkali phosphates, 0.387%; other salts, 2.428%; total ash, 3.152%.

[3] "Structure of the Cotton Fiber," p. 147.

undergone. Thus cotton waste may contain a considerable amount of foreign material and dirt as well as oil and starch. The oil is, in part, a different kind to that found in raw cotton and may be traced to the machinery in which the cotton fiber has been spun. Starch may often be traced to the previous use of sizing agents.

According to Lefevre,[1] the following represent typical analyses of mercerized Egyptian cotton:

Kind of Cotton	Per Cent. Ash	Per Cent. Iron Oxide in Ash	Color of Ash
Natural Egyptian	0.624	1.50	White
Mercerized Egyptian	0.137	8.02	Greenish
Grey mercerized Egyptian	0.403	2.31	Yellowish gray
Bleached mercerized Egyptian	0.088	5.45	Greenish

A. Viehoever[2] is authority for the statement that Upland cotton, *Gossypium hirsutum*, contains quercimeritrin and isoquercitrin, which have been previously isolated from other types of cotton plant, but does not contain gossypitrin and gossypetin. The ethereal oil isolated from Upland cotton differs from that found in the root back of *G. herbaceum*. The greater part distils between 200° and 300°, the lower fractions of the distillate being yellow to greenish yellow, and the higher fractions light bluish green to dark blue. The oil is said to attract the boll weevil.

Tissue Paper. It is generally conceded that the finest qualities of pyroxylin lacquers, bronzing fluids and transparent colorless pyroxylin plastics can only be obtained by the nitration of fine tissue paper, and it is a fact, that at the present time in the United States at least, substantially all of the celluloids are manufactured from tissue paper rather than linters or other forms of cotton cellulose. It is also a fact that best results up to the

---

[1] Rev. gén. mat. color. 1909, **13**, 281; abst. C. A. 1910, **4**, 251; Rep. Chim. 1910, **10**, 30; Zts. ang. Chem. 1910, **23**, 79. For the presence of iron in mercerized cotton see L. Lefevre and E. Blondel, Rev. gén. mat. color. 1909, **13**, 313; abst. J. S. C. I. 1909, **28**, 1192; C. A. 1910, **4**, 386; Rep. Chim. 1910, **10**, 130; Zts. ang. Chem. 1910, **23**, 235.

[2] A. Viehoever, L. Chernoff and C. Jones, J. Agric. Res. 1918, **13**, 345; abst. J. S. C. I. 1918, **37**, 485-A; C. A. 1918, **12**, 1562; J. C. S. 1918, **114**, i, 367. In this connection see Perkins, J. C. S. 1909, **95**, 1855, 2181; 1916, **109**, 145.

present time have been obtained from cellulose acetates esterified from tissue paper as the source of cellulose. The main advantages observed are ease and completeness of esterification, facility of clarification of the esterified cellulose by paper or plate filtration, water white solutions being invariably produced. The statement has also been made, that in the formation of nitrocellulose plastics typified by celluloid, less of the plastifying agent is required for colloiding purposes, where tissue paper is nitrated rather than cotton.

The color of nitrated paper is influenced greatly by the purity of the water used in the several processes of paper purification preliminary to esterification. Where the water used is unusually free from organic matter obtained from leaf mold, and from filtration through decaying vegetable matter or ferruginous strata, the final nitrated or acetated paper gives correspondingly clearer and lighter colored solutions when dissolved in the usual solvents and solvent conbinations.

Paper pyroxylin is considered essential to the celluloid manufacture in the preparation of transparent celluloid sheets, and for high class cinematographic and other continuous photographic films, where freedom from specks is absolutely necessary on account of the high magnification to which the film is necessarily subjected to when thrown upon the screen. Another point of importance is, that the extreme thinness of tissue paper renders nitration apparently more uniform, and in the case of acetation, tissue paper more readily disintegrates in the acetylating bath and hence esterifies more uniformly and quickly. The paper, of course, must consist of pure cellulose without loading, and should not be calendared. So-called "grass bleached" paper is preferred for nitration for the celluloid industry, and also for the manufacture of cellulose acetate.

O. Kress and S. Wells[1] have pointed out the value of cotton linters and shavings as paper making materials, and report the varying conditions of manufacture as influencing the quality of the finished paper.[2]

---

1. Paper, 1919, **24**, 569; abst. C. A. 1919, **13**, 1927.
2. They state that (1) with shavings, 12 lbs. of caustic soda are required for cooking 100 lbs. of dry shavings at 100 lbs. pressure for 4 hours. The yield is 70% and the bleach not over 4%, calculated, as bleaching powder with 35% available chlorine. On account of the loss of fine fiber in wash-

The nitrating processes of J. Hyatt,[1] M. Delpy,[2] Darapsky,[3] G. Mowbray,[4] V. Pallotti,[5] S. Emmens,[6] E. Liesegang,[7] Selwig and Lange,[8] and J. Swan,[9] were all designed for tissue paper and are described in detail elsewhere in this work. The processes of G. Melland[10] and J. Clouet,[11] may also be mentioned.

Cotton Wax. The substance known as cotton wax was first isolated by E. Schunk from East Indian and Middling Orleans cotton.[12] His method of extracting the wax consisted in boiling a large quantity of carefully spun cotton yarn in amounts varying from 450 to 2400 lbs., in a kier with soda ash for $7^1/_2$ hours, acidulating the dark brown kier liquor with sulfuric acid filtering and washing the resulting light brown flocculent precipitate, from which he extracted the wax by boiling alcohol. He described the product as a wax-like substance, melting at 86° and closely resembling

---

ing, the yield of paper from shavings was 55% based on bone-dry weights. (2) With cotton linters, 9 lbs. of caustic soda are required to cook 100 lbs. of bone-dry materials at 100 lbs. for 4 hours. The yield is 90% of bone-dry pulp, which can be satisfactorily bleached with not over 2% bleach. Bleaching and washing losses will reduce the yield of finished paper to 70%. (3) Hull fiber can be successfully pulped with 18 lbs. of caustic soda or a total of 15 lbs. of caustic soda and sodium sulfide per 100 lbs. of material by boiling at 90 lbs. for 3–4 hours. A pulp yield of 65%–75% is obtained and the pulp can be satisfactorily bleached with 5%–8% bleaching powder. Washing and bleaching losses reduce the final yield of paper to 47%–51%, all yields being calculated to the bone-dry weight basis. Photomicrographs and tabulated data are presented.

1. U. S. P. 210611, 1878. D. R. P. 3392, 1878; abst. Tech. Rep. 1878, 29; Dingl. Poly. 1879, **232**, 520.
2. F. P. 458558, 1913; abst. J. S. C. I. 1913, **32**, 1063. D. R. P. 256788, 1912; abst. C. A. 1913, **7**, 2116; Chem. Zentr. 1913, **85**, I, 1080; Chem. Ztg. Rep. 1913, **37**, 144; Wag. Jahr. 1913, **59**, I, 438; Zts. Schiess. Spreng. 1913, **8**, 138.
3. Dingl. Poly. 1865, **175**, 357, 451; abst. Jahr. Chem. 1865, **18**, 784.
4. U. S. P. 350497, 350498, 1886; abst. J. A. C. S. 1886, **8**, 239.
5. Ital. P. 34559, 1913.
6. E. P. 3852, 1890; abst. J. S. C. I. 1891, **10**, 484.
7. "The College Courant," February 26, 1870.
8. F. P. 409220, 1909; abst. J. S. C. I. 1910, **29**, 751; Mon. Sci. 1910, **73**, 295.
9. E. P. 21729, 1894; abst. J. S. C. I. 1895, **14**, 1062.
10. Mechanic's Mag. April 13, 1866; abst. Jahr. Chem. 1866, **19**, 859; Dingl. Poly. 1866, **181**, 150; D. Ind. Ztg. 1866, 175; Chem. Tech. Rep. 1866, **5**, I, 101; Elsner Mitth. 1866–1867, 249; Cosmos, 1866, (2), 101.
11. Dingl. Poly. 1877, **226**, 646; abst. Jahr. Chem. 1877, **30**, 1223; Bull. Soc. Rouen, 1877, 36; Pap. Ztg. 1877, 462; Chem. Tech. Rep. 1877, **16**, I, 288; Zts. fur Chem. Grossgewerbe, 1877, **2**, 778.
12. Mem. Man. Lit. and Phil. Soc. 1868, (3), **4**, 95; Chem. News, 1868, **17**, 118; 1874, **29**, 5; Bull. Soc. Chim. 1868, **10**, 70; Chem. Centr. 1868, **39**, 113; 1869, **40**, 112; Jahr. Chem. 1868, **21**, 980; Wag. Jahr. 1868, **14**, 614; Poly. Centr. 1868, **34**, 1006; Dingl. Poly. 1868, **188**, 496; Schwiez. poly. Zts. 1868, 121; J. de Pharm. (4), **8**, 232; Deut. Ind. Ztg. 1868, 252.

the wax extracted by Avequin from the leaves of sugar cane and carnauba wax extracted from the leaves of the Carnauba Palm. By saponification he was able to obtain from it a small quantity of cerosic acid. Schunck obtained in this manner from the cotton only 0.004% of wax which was insoluble in water, but soluble in alcohol and ether. He succeeded in isolating from the alcoholic extract a small quantity of a fatty acid which he identified as margaric acid, and which fused at 53°.

E. Knecht and J. Allan,[1] by extraction of raw cotton in a Soxhlet by means of benzol, have obtained 0.38% of crude cotton wax from Bengal cotton, 0.47% from Egyptian and 0.05% from American cotton. They were able to separate the crude wax into two fractions, designated by them cotton wax "A" and cotton wax "B." The former extracted by petroleum, boiling between 55°–65° was odorless, of a dull, yellow color closely resembling beeswax in texture and structure, though somewhat softer and much more sticky when softened by heat. The following constants were obtained:

Melting point, 66°–67° C.
Acid No. 44.1; equals 22.2% calculated as oleic acid.
Saponification value, 84.3; equals 664.2 saponification equivalent.
Iodine value, 28.35.

On repeated treatment with boiling 96% alcohol, 18.82% of the wax remained insoluble.

Cotton wax B: Dark green, almost black, granular plastic mass of complex nature, giving the following constituents:

Melting point 68°.
Acid No. 4.05; equals 2.03% calculated as oleic acid.
Saponification value 83.3, equals 671.5 saponification equivalent.

E. Knecht[2] exhaustively extracted raw Egyptian cotton-sliver with benzene yielding 0.47% crude cotton wax, having the appearance and consistence of beeswax. The Egyptian cotton deprived of wax yielded on extraction with alcohol 0.68% of solid extract, amorphous, very hygroscopic and of a dark brown color. Aqueous extraction which followed gave 1.46% of a brown, hygroscopic substance similar to the alcoholic extract.

Texas cotton yielded 0.55% of crude wax soluble in benzene.

---

[1] J. Soc. Dyers Col. 1911, **27**, 142; abst. C. A. 1911, **5**, 3911; J. C. S. 1911, **100**, ii, 645; J. S. C. I. 1911, **30**, 813; Meyer Jahr. Chem. 1911, **21**, 448, 514; Wag. Jahr. 1911, **57**, II, 428; Zts. ang. Chem. 1911, **24**, 2183.

[2] Text. Inst. 1911, **2**, 22; abst. C. A. 1912, **6**, 935; J. S. C. I. 1911, **30**, 1007; J. Soc. Dyers Col. 1911, **27**, 254.

The alcoholic extract amounted to 0.90% and contained 1.07% of nitrogen; reduced Fehling's solution strongly; while the aqueous extract was 1.61%; the ammoniacal extract 0.39% and the formic acid extract 0.72%. When the exhausted Texas cotton was digested with cold dilute HCl it yielded a further 0.43% of exextract. Bengal cotton yielded but 0.38% crude wax. Innumerable samples of raw cotton cloth have been examined by M. Freiberger[1] for fat content, the results varying within wide limits, according to the quality of the cotton. In the preliminary desizing generally practiced by the bleacheries with soap, the fats are largely split. In the bowking liquors from several bleacheries, considerable difference in the quantitative and qualitative character of the fatty acids were observed. Chemicking and souring were found to change the remaining fatty substance by the oxidization action of the chlorine.

C. Piest[2] has subjected raw American cotton (linters) to extraction with the following solvents in a Soxhlet apparatus: benzene, petroleum ether, ethyl ether and absolute alcohol. The following table gives the results obtained:

				Alcohol Extract	
Ether Extract %	Benzene Extract %	Petroleum Ether Extract %	%	Saponification Number	Iodine Value
0.74	0.87	0.50	1.27	159	22.1

The iodine value of the cotton wax obtained (22.1) is close to that found by Knecht and Allan (28.5) for the cotton wax which they obtained by extracting raw Egyptian cotton with petroleum ether. The quantity of so-called wood gum (probably xylan) present in the raw cotton, was found to be 1.32% and was obtained by extraction with cold 5% caustic soda solution. The copper number as determined by Schwalbe's method was 3.57.

Cotton was also examined after it had passed through the normal purification process used in preparing it for nitration.

---

[1] Farber. Ztg. 1915, **26**, 295; abst. C. A. 1916, **10**, 2304; Chem. Zentr. 1916, **87**, I, 446. In this connection see M. Freiberger, Zts. anal. Chem. 1917, **56**, 229; abst. J. S. C. I. 1917, **36**, 923; Ann. Rep. Soc. Chem. Ind. 1917, **2**, 127.

[2] Zts. ang. Chem. 1912, **25**, 396; abst. Chem. Zentr. 1912, **83**, I, 1643; C. A. 1912, **6**, 1688; Chem. Ztg. 1913, **37**, 753; abst. J. S. C. I. 1913, **32**, 694; C. A. 1913, **7**, 3545; Chem. Zentr. 1913, **84**, II, 550. See also Zts. ang. Chem. 1912, **25**, 2518; abst. Chem. Zentr. 1913, **84**, I, 1145; J. C. S. 1908, **94**, i, 138; C. A. 1913, **7**, 895.

The process consisted first in the mechanical purification; second in heating with dilute caustic soda solution under pressure; and, finally, washing with dilute normal hydrochloric acid solution: Nine samples of such prepared cotton were investigated in duplicate. The ether extracts ranged from 0.09% to 0.36%; carbon tetrachloride extracts from 0.12% to 0.31%; the alcohol extract from 0.23% to 0.52%. The lowest "wood gum" or xylan content found was 0.33% and the highest 0.89%. The copper numbers were found to be roughly proportional to the xylan content. In another series of experiments a sample of the prepared cotton was taken and extracted with the three solvents in succession, the results of the typical experiments being tabulated below.

ETHER EXTRACT

%	Saponification Value	Iodine Value
0.12	180.0	10.37
0.13		

TETRACHLORIDE EXTRACT AFTER THE ETHER EXTRACTION

%	Saponification Value	Iodine Value
0.09	231.7	6.60
0.14		

ALCOHOL EXTRACT AFTER THE TETRACHLORIDE EXTRACTION

%	Saponification Value	Iodine Value
0.23	149.5	7.40
0.29		

The experiments indicate that the copper number is increased by the presence of cotton wax.

Absorbent Cotton, is cotton which generally is suitable for nitration, irrespective of preliminary processes of purification to which it may have been subjected. Absorbent cotton is merely, of course, purified cotton in which the ether extract (fat) is seldom more than four-tenths of one per cent., which cotton will almost immediately sink when immersed in water.

According to A. Chaplet,[1] in the absorbent cotton industry in France, the cotton is first given a 12 to 48 hour bath in 1% caustic soda under slight pressure, then chemicked for 20 min-

---

[1] Rev. chim. Ind. 1914, **25**, 117; abst. C. A. 1914, **8**, 2951. L. Warneke (Phot. Mitth. No. 177, 239; Chem. Ztg. 1879, **3**, 198; Chem. Tech. Rept. 1879, **8**, I, 288) has described a method of producing absorbent cotton especially suitable for the manufacture of cellulose esters. The J. Pierce method of producing absorbent cotton is described in U. S. P. 239398, 1881

utes, washed, soured and washed again. It is then submitted to a weak sodium hydrate bath, washed, soured, and well washed, squeezed and quickly dried. Sometimes an antichlor is used, but unless great attention is given to its application, the white color is apt to take on a yellowish tinge after standing.

The French tests for suitable absorbent cotton are that it should be neutral to all indicators, should sink at once in cold water and leave less then 0.2% ash, and should show less than 0.5% of combined ethereal-ethyl alcoholic extract.

In the judgment of F. Kilmer,[1] absorbent cotton should preferably be made from the type of cotton known as Texas Strict Middlings, as other grades are apt to give inferior results. An unbleached absorbent cotton, largely used on the Continent, is made by similar extraction of the fiber mass by the aid of solvents. The best bleached product, according to Kilmer, is made as follows: washing in water, slight alkaline hydrolysis consisting of a boil with 1% caustic soda for 12 to 48 hours under low pressure; washing; then oxidation with hypochlorite of lime or soda, the latter being the better, the action is prolonged, the solution containing about 0.1% of chlorine, this treatment being continued until the cellulose is sufficiently oxidized to show the oxycellulose reaction. Then follows hydro-extraction, acid treatment in a 2% solution of sulfuric acid, washing and hydro-extraction followed by a second alkaline hydrolysis, this time consisting of a short boil with 0.25 caustic soda, washed, hydro-extracted, treated with antichlor or a solution of soap, followed by final washing. Of course sterilizing by steam or rendering antiseptic by means of treatment with formaldehyde gas is never resorted to in the preparation of cotton intended for nitrating purposes.

According to J. Garcon,[2] Sea Island and Egyptian grades of cotton, with their fine and long fibers are not suitable for the preparation of absorbent cotton as it is very difficult to make them absorbent. Brazilian cotton is too woolly and when colored,

---

[1] J. S. C. I. 1904, **23,** 967; abst. J. Soc. Dyers Col. 1905, **21,** 19; Chem. Centr. 1904, **75,** II, 1752; Chem. Ztg. 1904, **28,** 363. C. Dodge, Sci. Amer. Suppl. 1910, **69,** 358.

[2] Textile Mfg. **31,** 387; abst. J. Soc. Dyers Col. 1906, **22,** 103. In the Amer. Druggist, 1907, **50,** 136, are reported the analyses of 15 samples of absorbent cotton, the fatty matter therein ranging from 0.32%–0.98%. See J. Gilmour, Year Book Pharm. (Lon.) 1907, 446. K. Helfritz, Pharm. Zentralh. 1910, **51,** 101; abst. Chem. Zentr. 1910, **81,** I, 1163.

difficult to bleach. Indian cotton is little used because of its tender and dirty fiber. The best grades are those of New Orleans, Texas, Allen Seed, Mobile and Benders of Middling Grades. Unripe fibers, dead cotton, and those to which the seed is attached must be removed because they do not possess the cellular canal and are therefore not absorbent. They become brittle when treated chemically. Cotton card waste is suitable for use but usually does not yield a high class article. On the Continent, absorbent cotton is obtained by removing all trace of fatty matters by means of volatile solvents.

Garcon shows that the operations necessary in the preparation of absorbent cotton can be divided into the mechanical operation, such as sampling, sorting, cleaning, picking and carding; chemical operations, such as boiling, washing, treatment with alkaline solutions; bleaching and drying, acidifying and drying, a second treatment with alkali, acidifying, neutralizing and finally drying. The mechanical operations embrace cleaning and drying at 105°, carding and winding on spools. Care should be taken in the use of absorbent cotton for nitration that it has not been overbleached, as often the chemical treatment to which it is subjected is unnecessarily harsh.

In bleaching with sodium hypochlorite or with calcium hypochlorite, the process is usually carried much further than is the case with ordinary chemicking and this is the reason why absorbent cotton has increased affinity for basic dyes, which affinity can be used as a test of the absorbing power of cotton. The removal of acids is one of the most important features of the process and is difficult unless great attention be paid to seemingly unimportant details.

V. Vaughan is authority for the statement that approximately 25,000 short tons per annum of absorbent cotton was recoverable from the hospital and medical units on the allies' front, provided such material is suitable for the production of nitrocellulose or the cellulose esters and provided also that it would be delivered and purified at a cost not greater than that of the present market price for cotton linters and hull fibers. Of course, in connection with this suggestion is the possibility of traces of mercuric chloride remaining in the used cotton from the antiseptics employed, traces of mercuric chloride, as it is well known, have a tendency to mask the stability tests of the finished nitrocellulose.

In the Ninth Revision of the United States Pharmacopeia, absorbent cotton is officially described as follows:

"Purified cotton occurs in white, soft, fine filaments, appearing under the microscope as hollow, flattened and twisted bands, spirally striate, and slightly thickened at the edges; inodorous and almost tasteless; insoluble in ordinary solvents, but soluble in an ammonia solution of cupric oxide.

When purified cotton, previously compressed in the hand, is thrown on the surface of cold water, it readily absorbs the latter and sinks.

Incinerate 5 gm. of purified cotton; not more than 0.2% of ash remains.

Thoroughly saturate about 10 gm. of purified cotton with 100 mils of distilled water, then with the aid of a glass rod press out two portions of the water, 25 mils each, into white porcelain dishes. Add to one portion 3 drops of phenolphthalein T. S. and to the other portion 1 drop of methyl orange R. S.; no pink color develops in either portion (alkali or acid).

Extract 5 gm. of purified cotton, tightly packed in a narrow percolator, with ether, until the percolate measures 20 mils, and evaporate this to dryness; the residue does not exceed 0.6 per cent. (fatty matter).

Extract 10 gm. of purified cotton, in a narrow percolator, with alcohol, until the percolate measures 100 mils. When observed downward through a column 20 cm. in depth, the percolate may show a yellowish color, but no blue or green tint (dyes); and, on evaporating this percolate to dryness, the weight of the residue does not exceed 0.5 per cent. (resins and soap)."

F. Kilmer has recorded in detail the methods of preparation of cotton fiber for surgical purposes, in which condition it is especially suitable for either nitration or acetation, when deprived of substantially all of its atmospheric moisture. In the preliminary treatment of cellulose for technical purposes, E. Berl[1] advo-

---

[1] Zts. Schiess Sprengst. 1909, **4**, 81; abst. J. S. C. I. 1909, **28**, 380; C. A. 1909, **3**, 1926; Chem. Zentr. 1909, **80**, I, 1275; Jahr. Chem. 1909, **62**, 384; Chem. Tech. Rep. 1909, **33**, 194; Wag. Jahr. 1909, **55**, I, 431. For information concerning errors in appraisement of absorbent cotton, refer to Morenl, Bol. chim. farm. **51**, 151; abst. C. A. 1912, **6**, 2817.

cates the reduction in the viscosity of the esterized cellulose, either by a depolymerization of the cellulose, mercerization, or regulated hydrolysis before esterification.

Methods of Cotton Analysis.[1] 1. *Specifications:* The usual smokeless powder specifications require the use of bleached cellulose containing not more than 0.4% of extractive matter; not more than 0.8% of ash; and state that it should not contain more than "traces" of lime, chlorides and sulfates. For some commercial grades of nitrocellulose, unbleached cotton is used, but the methods of analysis are the same as for bleached cotton. The routine analysis of cotton includes the determination of moisture, ether extract, ash, solubility in 95% sulfuric acid and solubility in 10% caustic potash. The furfural value is also figured in the determination and on crude fiber the amount of "dust" is determined by a sieving test as described.

2. *Sampling:* In sampling fiber in bales, a section extending from one side to approximately the center is taken from each bale sampled, the samples being taken from not less than one-tenth of the number of bales in the lot. In sampling crude fiber, special note should be made and samples taken of any bale showing large proportions of mouldy fiber or of very oily fiber as indicated by a pronounced yellow color. The samples for moisture are quickly and thoroughly blended by hand and a sample of about 20 gm. placed in a previously weighed glass or in a vessel with tightly fitting cover. The remainder of the sample is opened up by hand or in a mill or picker if available, and after being thoroughly blended is reduced to proper size by quartering and dried at 105° C. All determinations except moisture and dust are made on the dry sample.

3. *Moisture:* About 20 gm. of a sample prepared for moisture determinations are weighed under conditions to avoid changes in moisture content, dried at 105° for three hours, or, if the moisture is high, as may happen with samples taken from bales that have lain out in the rain, heating is continued until constant weight is reached. The loss in weight is calculated to the per cent. of the sample as received.

4. *Ash:* At least 5 gm. of dry material, prepared as above,

---

[1] This is supplementary to the general topic in Chap. I, and especially applicable to cotton cellulose.

is placed in a platinum or silica dish of 80 to 100 cc. capacity, moistened with a small amount of pure nitric acid, covered, and heated on the water bath until active decomposition ceases. Incineration is then completed at a low red heat, care being taken to avoid loss of ash and to keep the incineration below the vaporizing point of the alkali chlorides. The dish is then cooled, the ash moistened with a few cubic centimeters of distilled water, and after evaporating the water on the steam bath or hot plate, the ash is again heated to a low red heat. This procedure causes the ash to deposit on the dish in a small layer which is not affected by air currents through handling. Under these conditions the ash is largely in the form of carbonate. The dish and contents are finally cooled in a desiccator and weighed and the result calculated to the per cent. of dry weight of the cotton. The powder specifications usually call for the digestion of a 1.5 gm. sample with a little pure nitric acid, and incineration at a red heat. The use of a smaller sample of cotton and a higher temperature of incineration are likely to give too low results.[1]

5. *Ether Extract:*[2] About 5 gm. of dry material are thoroughly extracted with pure ethyl ether in a suitable extraction apparatus (preferably that of Knorr's) for about eight hours or until further extraction removes no additional substances soluble

---

[1] E. Justin-Mueller has pointed out (l'Ind. chim. 1918, **5**, 218; abst. C. A. 1919, **13**, 74) that of the non-cellulosic matters particularly the cuticle or epidermis, is not dissolved but is carbonized and remains with the insoluble mineral compounds which are determined as "ash." These consist largely of calcium phosphate and carbonate, and an error may enter into this determination through the action of the sulfuric acid converting them into sulfates. These compounds, which amount to 25% of the weight of insolubles in a cotton of good quality, are increased to 32.59% by the treatment with sulfuric acid. Mueller details the method of calculation to be followed to avoid this error. The tests determined were as follows: (1) The percentage of waste; (2) the tensile strength of the yarn; (3) the bleaching properties of the yarn and cloth; (4) the moisture content; and (5) other manufacturing properties of the cotton. The sources of the samples, method of sampling, methods and conditions of the various tests employed to determine the 5 factors above mentioned, are described in detail and the results assembled in 10 tables and 11 charts. The tests show that after making allowance for the losses due to the cleaning process there is comparatively little difference between the grades above and those below Middling in the price paid by the manufacturer for each pound of usable cotton obtained from bales of different grades, but that there is a difference in the intrinsic value per pound of the manufactured product.

[2] G. MacNider (Proc. Assoc. Off. Agrl. Chem. 1910, 155; Bull. 137, U. S. Dept. Agr.) has presented a comparison of petroleum ether and ethyl ether for determining fat in cotton products.

in ether. The extractive matter is weighed after drying at 100° to constant weight and the result (after deducting the weight of the residue in the ether in a control experiment) is calculated to the per cent. of dry weight of material. Care must be taken to have the extractive matter free from even particles of fiber which may be present there mechanically. After extraction with ether the sample may be dried and used for the determination of non-cellulose, as below.

6. *Solubility in Sulfuric Acid.—Determination of Non-cellulose:* The sulfuric acid used must be within 0.1% of 95% absolute acid. The determination is made by treating five grams of dry cotton at about 20° with 50 cc. acid at the same temperature. In the case of crude fibers it is important to remove the oils by extraction with ether before making this determination. The fiber is stirred vigorously in the acid for five minutes, then slowly poured in ten liters of cold distilled water. The aqueous solution is heated on a hot plate for at least four hours, with frequent stirring, keeping the temperature as near as possible to 100°. The insoluble matter is filtered out on a Gooch crucible with a carefully prepared asbestos mat. The contents of the Gooch are thoroughly washed with boiling distilled water to remove the last traces of sulfuric acid and then dried for three hours at 100°, cooled and weighed, and the result calculated to the per cent. on the dry weight taken. It is important to use asbestos for the Gooch that does not lose weight when treated with dilute sulfuric acid. It is also important that the fiber is well opened up and free from lumps, for if lumps are present a higher result may be obtained.

7. *Approximate Cellulose:* The approximate cellulose in the fiber is found by adding together the percentage of ash, ether extract, and non-cellulose, and subtracting the total from 100%.

8. *Solubility in Caustic Potash:* Cellulose is insoluble in alkalis, so that in the crude fiber, solubility in caustic potash is a measure of the non-cellulose present. In the purified fiber it is a measure of the severity of the bleaching and indicates the amount of hydrocellulose and oxycellulose present. A solution of pure potassium hydroxide of a concentration within 0.1% of 10% is prepared by dissolving the proper weight of the purest

obtainable potassium hydroxide in distilled water. The strength of the solution is to be carefully checked by titrating and it must be carefully protected from carbon dioxide.

Approximately two grams of the sample are dried in a wide mouthed weighing bottle to constant weight at 102°–105°, the contents of the bottle transferred to a 250 cc. Jena glass beaker, covered with 100 cc. of 10% potassium hydroxide solution, the beaker covered with a watch glass and the contents heated to 100° for three hours. Heating on the steam bath is unsatisfactory for this purpose as it does not give a sufficiently high temperature. Care must be taken to avoid concentration of the solution or undue oxidation of the fiber due to exposure of the alkali-soaked fiber to the air. It is also necessary that the temperature be kept as close to 100° as possible, since variations in temperature materially affect the resultant material. After the heating is completed, the contents of the beaker are poured into a flask containing one liter of distilled water and any residue in the small beaker is washed into the other. The alkali is then neutralized with a decided excess of acetic acid, this excess of acid being necessary in order to break up the combination of alkali and cellulose. The undissolved cotton is then filtered into a weighed Gooch crucible having an asbestos mat, is thoroughly washed successively with hot water, then alcohol, and finally ether. It is then rapidly dried to constant weight at 102°–105°. The loss of weight of material is calculated to per cent.

In making this determination on crude fiber the amount soluble in hot water alone is deducted from the total and expressed separately and a further correction must be made for the oils extracted by ether and the per cent. of ash which goes into solution in the acetic acid, though these corrections are not necessary on the bleached fiber. In order to determine the amount of ash which goes into solution, the ash determination must be made on the fiber after treatment.

9. *Furfural Value* (Pentosans).—*Preparation of Reagents:* The purity of the phloroglucinol is tested by dissolving a small quantity in a few drops of acetic anhydride heating almost to boiling and adding a few drops of concentrated sulfuric acid. A violet color indicates the presence of diresorcinol. If the phloroglucinol gives more than a faint coloration it should be purified

by the following method:

Heat in a beaker about 300 cc. of hydrochloric acid (sp. gr. 1.06) and 11 gm. of commercial phloroglucinol added in small quantities at a time, stirring constantly until it has almost entirely dissolved. Some impurities may resist solution but it is unnecessary to dissolve them. Pour the hot solution into a sufficient quantity of the same hydrochloric acid (cold) to make the volume 1500 cc. Allow it to stand at least over night, better several days, to allow the diresorcinol to crystallize out and filter immediately before using. The solution may turn yellow but this does not interfere with usefulness. In using it, add the volume containing the required amount to the distillate.

Determination: Place a quantity of the material, chosen so that the weight of the phloroglucinol obtained shall not exceed 0.300 gm. in a flask together with 100 cc. of 12% hydrochloric acid (sp. gr. 1.06) and several pieces of recently heated pumice stone. Place the flask on a wire gauze, connect with a condenser, and heat rather gently at first and so regulate as to distill over 30 cc. in about 10 minutes, the distillate passing through a small filter paper. Replace the 30 cc. driven over by a like quantity of the dilute acid added by means of a separatory funnel in such a manner as to wash down the particles adhering to the sides of the flask and continue the process until the distillate amounts to 360 cc. To the completed distillate gradually add a quantity of phloroglucinol (purified if necessary) distilled in 12% hydrochloric acid and thoroughly stir the resulting mixture. The amount of phloroglucinol used should be about that of the furfural expected. The solution first turns yellow, then green and very soon an amorphous greenish precipitate appears, which grows rapidly darker, till it finally becomes almost black. Make the solution up to 400 cc. with 12% hydrochloric acid, and allow to stand over night.

Filter the amorphous black precipitate into a tared Gooch crucible through an asbestos felt, wash carefully with 150 cc. of water in such a way that the water is not entirely removed from the crucible until the very last, then dry for four hours at the temperature of boiling water, cool and weigh, in a weighing bottle, the increase in weight being reckoned as phloroglucinol, using the following formulas given by Kroeber:

(a) for weight of phloroglucinol "w" under 0.030 gm., furfural equals (w ÷ 0.0052) times 0.5170.

(b) for weight of phloroglucinol "w" over 0.300 gm., furfural equals (w ÷ 0.0052) times 0.5180.

For weight of phloroglucinol "w" from 0.030 gm. use the following formula:

Furfural equals (W ÷ 0.0052) times 5185.

10. *Determination of Copper Value:* In order to insure that the cotton has not been over-bleached and is reasonably free from oxycellulose and other reducing substances, the "copper value" may be determined. The results obtained by this depends to a large extent upon the exact procedure in carrying out the test, but a standard method has been worked out by Schwalbe as follows: 3 grams of air-dry cotton are cut into small pieces and mixed with 200 cc. water and 100 cc. Fehling's solution. This blue liquid is actively boiled for fifteen minutes under a reflux condenser by means of a water-glycerol bath[1] with frequent agitation, the time being reckoned from the moment when full ebullition commences. The liquid is filtered with the aid of a suction pump through a Gooch crucible with asbestos mat and the residue containing cuprous oxide is washed with boiling water until the filtrate is colorless. The copper oxide is then dissolved in nitric acid and the amount of copper determined, preferably, electrolytically. The "copper value" is the percentage of metallic copper, calculated on the dry cotton sample.

Or, after the heating the liquid is filtered, and the precipitate after washing first with water, then with Rochelle salt solution, and finally with water, is dried and ignited. The ash is dissolved in a few drops of nitric acid, the solution warmed and then diluted, made slightly alkaline with sodium bicarbonate, and then just brought back to neutrality with acetic acid.

Excess of KI is added and the liberated iodine titrated back with $N/10$ sodium thiosulfate, the copper equivalent of the iodine found being calculated as cuprous oxide.

The following results are given by Schwalbe as obtained from various materials:[2]

---

[1] The composition of water and glycerol in this bath is so adjusted as to give a boiling temperature of 105°, which is usually equivalent to 100° inside the flask.

[2] According to E. Hägglund (Papierfabr. 1919, **17**, 301; abst. Chem. Zentr. 1919, **90**, II, 296; J. S. C. I. 1919, **38**, 894-A), Schwalbe's method for

11. *Dyeing Test:* The presence of oxycellulose, as has previously been pointed out, is also indicated by the depth of color which certain basic dyestuffs, as fuchsine, impart to the cellulose fiber. This may be determined by immersing one gram of the sample to be tested in 100 cc. of a 0.2% fuchsine solution, the mixture being then gently boiled for 30 minutes. The cotton is then removed and washed, first with cold and then with hot water, until no further amount of color is extracted. The depth of color is an indication of the oxycellulose present.

12. *Viscosity Value.* H. Ost[1] has called attention to the

---

the estimation of the copper value may be simplified by using Bertrand's volumetric method for the titration of the reduced cuprous oxide. Four gm. of the finely disintegrated cellulose is stirred with 200 cc. of water, which is then heated to boiling, and 100 cc. of boiling Fehling's solution added. The mixture is boiled for 15 minutes and then filtered in a Neubauer platinum crucible or else on a double filter paper with the assistance of kieselguhr paste. The cellulose containing the cuprous oxide is washed with hot water and then treated with 100 cc. of boiling ferric sulfate solution containing 50 gm. of ferric sulfate and 200 gm. of sulfuric acid per liter. The iron solution should previously be tested for inertness towards permanganate. The cuprous oxide is thereby dissolved, and the cellulose is washed several times with boiling water. The filtrate is then titrated with $N/10$ permanganate, and shows a sharp end-point from green to pink. With regard to tests for the quality of unbleached Mitscherlich sulfite pulp, the author has determined the copper sulfate absorption values, but finds no connection between these and the bleaching capacity of the pulps. The bleaching quality, however, shows a more consistent relationship with the lignin value as determined by Klason's method. None of the usual chemical tests, such as copper value, hydrolysis value, etc., showed any satisfactory concordance with the strength and mechanical qualities of the cellulose. Only in certain very pronounced cases can any definite relation be found between the tensile strength and the degree of digestion of the pulp. It may frequently happen that a fully digested pulp is as strong as or stronger than an under-digested material.

Surgical cotton wool	1.64 to 1.8
Mercerized bleached Egyptian cotton	1.9 to 1.6
Glanzstoff artificial silk	1.1
Hydrocellulose	5.2 to 5.8
Parchment paper	4.2
Bleached sulfite wood pulp	3.9

[1] Zts. ang. Chem. 1911, **24**, 1892; abst. Wag. Jahr. 1911, **57**, II, 428; abst. J. S. C. I. 1911, **30**, 1247; C. A. 1912, **6**, 684; Chem. Zentr. 1911, **82**, II, 1518; J. C. S. 1911, **100**, i, 838; W. Dean and F. Taylor (U. S. Dept. Agr., Bull. **501**, 27 pp. (1917) have described in detail the manufacturing tests of the official cotton standards for grade, spinning tests being conducted for the purpose of determining the relative intrinsic values of cotton of the grades of Middling Fair, Good Middling, Middling, Low Middling, and Good Ordinary. M. Lahache (Union pharm. Mar. 15, 1915; Repert. pharm. 1916, **28**, 4; C. A. 1916, **10**, 950) has detailed simple tests for the principal constituents of medicated cotton and gauzes as well as physical qualifications for absorbent cotton and gauzes. For the testing of cotton by steaming, consult M. Freiburger, Färber Ztg. 1917, **28**, 221, 235, 249; abst. Zts. ang.

determination of the viscosity of solutions in cellulose in copper ammonia of definite composition as a means of distinguishing cotton and allowing conclusions to be drawn regarding its preliminary treatment.

13. *Viscosity Value* (*Woolwich Method*): The viscosity of cellulose is determined in cuprammonium solution, and it is of the utmost importance in order to obtain reliable results to use a cuprammonium solution prepared according to the standard method, and to avoid the action of light and air on the cellulose solution.

Preparation of the Cuprammonium Solution: 60 gm. of copper sulfate are dissolved in 1 liter of hot water in a wide necked bottle, a few drops of sulfuric acid being added. The solution is allowed to cool to 50° and ammonia (sp. gr. 0.880) added until the precipitation of basic copper sulfate is complete, any excess of ammonia being neutralized with a few drops of sulfuric acid. The precipitated basic sulfate is allowed to settle and the supernatant liquid decanted. The precipitate is washed by decantation with water at 80°, until the wash water is free from sulfate. 200 cc. of 20% caustic soda are then added and the whole well shaken at ordinary temperature. The precipitate is converted to blue cupric hydroxide which is then allowed to settle, the supernatant liquid decanted and the precipitate washed by decantation with cold water till the wash waters are free from alkali. The

Chem. 1918, **31**, 146; J. S. C. I. 1918, **37**, 408-A. L. Dewey and M. Goodloe (Bur. Plant Ind. Circ. 128-B, 17–21) have described a machine for testing the breaking strain of cotton fibers. B. Rogalski (Russ. j. l'agric. experimentale, 1916, **17**, 13; abst C. A. 1915, **10**, 3165) has reported analyses of cotton taken during the general stages of its evolution. Samples of cotton (*Gossypium hirsutum* L.) were taken during 4 stages of its growth: at the commencement of budding, at the commencement of flowering, at the time of harvest, and after frost. It was found that the amount of nitrogenous substances and the relative amount of nitrogenous non-albuminous substances decreased with the age of the plant. The same took place in the case of non-nitrogenous substances soluble in water, and in the case of the ashes. The latter are composed of chlorides and sulfates. The part solusoluble in acids consists largely of compounds of potassium. Parallel to the growth of the cotton, an accumulation of lignin and pentosans takes place in the cell walls. It is believed that pure lignin and hemi-cellulose are present at the same time in the fiber, and that complete hydrolysis of the hemi-cellulose is not obtained. This latter is evidently stable after boiling with 2% hydrochloric acid for three hours. A high amount of crude fat characterizes the green parts of the plant and the seeds, and their quantity generally depends on the % for the entire plant. The iodine number for the crude fat of parts of the pod other than the seed and fresh leaves leads to the belief that these capsules have not attained maturity.

precipitate is then transferred to a Büchner funnel and washed with distilled water and sucked dry. It is then dried on a porous plate in an air oven at 40°.

The dried cupric hydroxide is transferred to an aspirator bottle and 800 gm. of ammonia per liter are added. The whole is well shaken and the excess of cupric hydroxide allowed to settle. The supernatant liquid is run off through a glass wool filter and the volume measured. The copper in the solution is determined volumetrically and the theoretical quantity of ammonia, containing 200 gm. of ammonia per liter, is added to reduce the concentration of copper to 10 gm. per liter. The finished solution should be kept in a tightly stoppered aspirator bottle, and its copper content should occasionally be determined by titration.

Determination of Viscosity by Falling Sphere Method: The general arrangements are the same as for the determination of the viscosity of nitrocellulose solutions, but owing to the deep blue color of the solution it is necessary to use a tube of 1 cc. diameter.

In Fig. 1 is shown an apparatus for conducting this test, and consisting of a tube 1 cc. in diameter, about 30 cc. long with 5 graduations at 5 cc. intervals.

The water baths should be covered with brown paper with two vertical slits at opposite sides, and the head of the observer should be screened so that all light reaching him should pass through the blue solution.

Preparation of the Cellulose Solution: 2.1 gm. of air dried cotton cut up finely and degreased if necessary are weighed out, an allowance of 5% being made for moisture in all cases.

100 cc. of standard cuprammonium solution together with 8 or 9 glass beads are placed in a stout bottle of about 150 cc. capacity and the weighed quantity of cotton added. The bottle is then at once closed with an india-rubber stopper, through which a short capillary tube passes one end being flush with the bottom of the stopper, the other end being connected to a short length of india-rubber pressure tubing closed with a screw clip.

The pressure tubing is connected to a water pump and by opening the screw clip, the air in the bottle is displaced by ammonia evaporating from the solution. As soon as the bubbles reach the cork the screw clip must be at once closed and the bubbles are broken by a sharp tap given at frequent intervals.

This operation is repeated four times to ensure complete removal of the air from the bottle. The bottle is immediately shaken vigorously for five minutes and then at frequent intervals till solution is complete.

It is advizable to keep the bottle immersed in a covered bath of water at 20° C. as a protection for air and light.

Filling the Viscometer Tube: When solution is complete, the cork is removed from the bottle without disturbing the liquid and is replaced by a cord carrying a short inlet tube reaching to 1 cm. from the bottom and an outlet flush with the cord and about 50 cc. long.

The bore of the tubes is about 5 mm.

The viscometer tube is slipped over the long outlet tube and the bottle is then inverted carefully without shaking the liquid. The solution then flows down into the viscometer tube. When the tube is full, the outlet tube must be raised from the bottom of the viscometer tube, and care must be taken to avoid air bubbles forming in withdrawing it. It should not be raised above the surface of the liquid in the tube and the filling then proceeds further.

When the tube is filled to within 3 cc. of the top, the bottle is removed.

Determination of Viscosity: The tube is fitted with an india-rubber cork carrying a releasing tube. Care must be taken to place this centrally in the tube. It is then placed in position in the water bath and the viscosity determination carried out at 20° C.

In time of fall of a $^1/_{16}$ inch steel ball through 15 cc. is determined in the usual way.

Standardization of Viscometer Tube: The tube is standardized by taking the time of fall for castor oil of known viscosity.

Statement of Results: The time of fall through 15 cc. in a 1 cc. tube should be quoted. In addition the absolute viscosity should be calculated and quoted, as this allows for all corrections due to irregularities in the tubes which become important in tubes of 1 cc. diameter.

The absolute viscosity is given by the equation:

$$\frac{n}{n_1} = \frac{T(s - s^1)}{T_1(s - s^1)}$$

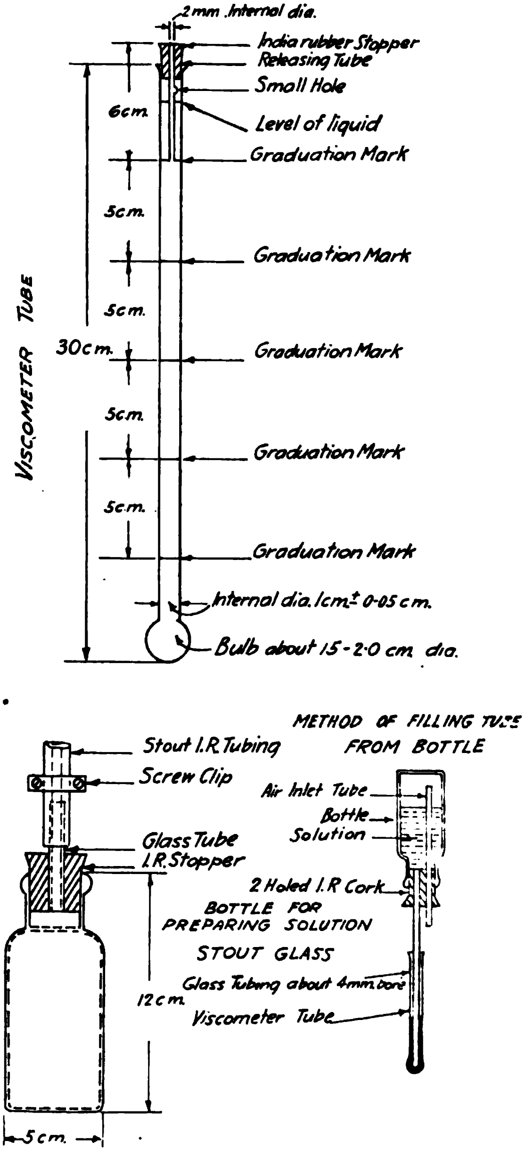


FIG. 1.—SPHERE VISCOSIMETER FOR CELLULOSE SOLUTIONS (WOOLWICH METHOD)

Tests of Cotton for Nitration purposes. Irrespective whether the cotton is in the form of waste, cop bottoms, linters or other short or long fiber, it should be as free as possible from foreign matter as string, pieces or metal or seed particles. The moisture should not exceed 7% or 8%. The oily matter is determined in the usual manner by extraction in a Soxhlet or similar apparatus with anhydrous ether, and whereas formerly as high as one per cent. ether extract was considered allowable, that permissible amount of fat is generally restricted to about 0.4% or less. To determine whether cotton has been over-bleached and reasonably free from oxycellulose and other reducing substances, it is subjected to a determination of the "copper value." A determination of the "alkali-caustic copper" will indicate as to whether the cotton has or has not been mercerized. The loss on boiling with caustic alkali under specified conditions should also be ascertained or the "wood gum" may be determined, but the insistence on low results by these tests has an incentive to the supplier to submit the cotton to prescribed treatment with alkalis whereby the cotton may readily be damaged.

An indication of the amount of oxycellulose is also determined by ascertaining the power of cotton to combine with basic dyestuffs such as magenta or methylene blue. Either the cotton may be treated with a dilute solution of a dye and well washed and the depth of color compared with that taken by a standard sample under comparable conditions, or the actual quantity of dye removed from the solution may be ascertained, the latter procedure being the more difficult.

G. Lunge and J. Bebie[1] soaked 0.5 gm. of cotton in 150 cc. of a 0.5% solution of methylene blue for one hour in a covered beaker on a boiling water bath. When cold, 100 cc. are poured off and the color compared with that of the original solution by means of a Lovebond tintometer or other colorimeter. In a typical experiment recorded, one gram of pure cellulose took up 0.0012 gm. of dyestuff.

Inspection of Cotton for Nitration Purposes. Professor Charles E. Munroe[2] has called attention to the fact that when

---

[1] Zts. ang. Chem. 1901, **14**, 510; abst. Chem. Centr. 1901, **72**, II, 34; J. C. S. 1901, **80**, i, 508; J. A. C. S. 1901, **23**, 527; Jahr. Chem. 1901, **54**, 893; Meyer Jahr. Chem. 1901, **11**, 316; Wag. Jahr. 1901, **47**, I, 495.

[2] J. A. C. S. 1895, **17**, 783; abst. Jahr. Chem. 1895, **48**, 1359; J. S. C.

converting cotton into nitrocellulose by immersion in mixed acid, it is essential that the cotton should rapidly absorb the acid, for if the portion that is taken for immersion be but slightly absorbent, it is quite likely that when but partly saturated, it will rise to the surface of the acid and on exposure undergo the rapid decomposition technically known as "firing," or "fuming off." To secure the desired result, therefore, the cotton should be free from oil, grease, or any protecting body. Their presence not only diminishes the absorptive power of the cotton but in common with the knots, tangles, cops, hulls, seeds, or similar formed bodies promote decomposition, decrease the speed of nitration, and result in the production of a body of deficient stability. Therefore in the determination of the relative value of various samples of cotton offered for purchase, the amount of the grease, foreign bodies and waste to be removed and of knots and tangles present, together with the general cleanliness of the sample given, are prime points for consideration. A method of inspection, therefore, should embrace the following:

1. Optical inspection for color, cleanliness, presence of cops, knots, tangles and foreign bodies and for relative length, appearance and strength of the fiber.
2. Odor and the presence of fungi and mold on the cotton filaments.
3. Moisture, as determined by drying a portion at 100° to 105° C. to constant weight.
4. Ether extraction as given in detail elsewhere herein.
5. Extraction with alkali.
6. Determination of ash.
7. Rate of absorption of water.

In making this latter test a sample of the material is thrown or dropped lightly on the surface of cold distilled water and the time noted between when it touches the surface and when (through absorption of the water by capillarity) it sinks to the bottom. One of the requisites for cotton suitable for the manufacture of

---

I. 1896, **15**, 214; Bull. Soc. Chim. 1896, **16**, 646; Chem. Centr. 1895, **66**, II, 1182. For use of cotton in the manufacture of explosives, see Nature, 1915, **95**, 481. For "Cotton as a High Explosive," consult B. Blount, Nature, 1915, **95**, 591. For the preparation of cotton for nitration, refer to H. Barthelemy, Le Caout. Guttap. 1913, **10**, 7353; abst. Kunst. 1914, **4**, 13; C. A. 1913, **7**, 4067.

nitrocellulose and smokeless powder is that it shall sink in two minutes.

In the samples examined by Munroe, the moisture varied from 3.38% to 8.40%; the ether extract from 0.0% to 7.10%; the caustic soda extract from 3.53% to 5.38%, and the ash from 0.05% to 1.79%. A sample of cotton seed lint gave moisture 6.16%; ether extract 2.35%; soda lye extract 28.54%; ash, 4.83%; A sample of waste cotton gauze gave moisture 7.37%; ether extract 0.50%; soda lye extract 3.89%; ash, 0.95%; rate of absorption, 7 seconds.

U. S. Ordnance Requirements for Cotton. The requirements of the Ordnance Department of the United States Army, as revised April 18, 1908, prescribe that the cellulose prepared for nitration, must be bleached cellulose which will be obtained by purifying unspun cotton waste and thoroughly washing to remove purifying materials or salts; containing not more than 0.7% extractive matter; not more than 1.25% of ash; of uniform character, and clean and free from such lumps as will prevent uniform nitration. The "extractive matter" is determined by extracting about 1.5 gm. of cotton in a Wiley extractor with ethyl ether, and weighing the extracted matter after drying at 100°. The percentage is calculated on dry cotton. Ash is determined by digesting about one gram of cotton with a little pure nitric acid and incinerating at red heat, being residue and calculated percentages on dry cotton. Moisture is determined by drying about three grams of cotton at 105° to constant weight.[1]

English Requirements for Nitrating Cotton. The specifications for cotton waste for the manufacture of guncotton (74/6/3623) are as follows: To be bleached cotton cellulose, specially suitable for the manufacture of guncotton.

To consist largely of fibers of long staple, preferably twisted; and to contain as little as possible of felted unspun short fiber cotton, or dust, technically known as "fly." The short lint obtained from the cotton seed after removal of the long staple cotton must not be used, however treated for purification. Spun

[1] Where large amounts of cotton are nitrated it is customary to send one bale in each 20 or 25 to the bale breakers, from which a representative sample is obtained. This is kept in a glass-stoppered bottle. Where a large number of bales are examined at one time, the individual samples are united by careful blending into one composite sample, and from this portions are withdrawn for analysis.

material such as cops or cop bottoms may be used. Weaving mill waste may not be used.

The waste must not show more than the following figures calculated as percentages on the dry material:

Moisture	7.0%
Oily matter	0.6%
Soluble on boiling 1 hour in 3% NaOH	5.0%
Reduction of Fehling solution (1 vol. to 2 vols. water on heating 15 minutes at 100° C. (Cu_2O)	1.0%
Mineral matter	0.5%
Starch	0.2%

Except as regards the above figures, it must be entirely free from organic matter other than pure resistant normal cellulose and, on dyeing with a basic dye such as Fuchsine (rosaniline acetate), the fixation of color must be slight and uniform and must show no deeply dyed particles or fibers.

(1) *Oil:* 5 gm. of the dry cotton to be extracted for four hours with 100 cc. ether in a Soxhlet extracting apparatus, and the ethereal solution evaporated. The residue must not exceed 0.8%.

(2) *Moisture:* 5 gm. dried in air bath at 100 C. must not lose more than 8%.

Specifications of Cotton for Nitration in Germany. According to Hertzog,[1] the military authorities specify a cotton suitable for nitration shall be one which, when thrown into water, sinks within two minutes; when nitrated, does not disintegrate; when treated with ether yields not more than 0.9% of fat, and containing only small traces of chlorine, calcium oxide, magnesium oxide, nitric oxide, sulfuric acid, and phosphoric acids.

The wastes from the spinning machine and lumps are purified by first boiling with caustic soda, under pressure, washing, bleaching with chlorine, washing, treating with sulfuric acid or hydrochloric acid, washing, centrifugalizing and then drying. When the cotton is very greasy it is first boiled with lime water. The loss in these several treatments varies considerably. For example, moisture 3 to 15 per cent., packing and in transit 2 to 5 per cent., boiling and washing 5%, and bleaching 1.5 to 2 per cent.

Cellulose used for Nitration. It has been stated, and probably correctly, that at least 95% of the cellulose nitrated consists

---

[1] Centr. f. Text. Ind. 1890, **21**, 975; abst. J. S. C. I. 1891, **10**, 161; Chem. Tech. Rep. 1890, **29**, II, 143; Chem. Ztg. Rep. 1890, **14**, 355.

of some form of cotton. In general the purer the cellulose used, the less difficulty in nitration and subsequent elimination of the acid, the higher the yield, and the more stable the nitrate formed. There is an economic limit, however, to the cost of the cotton which can be used, due to keen competition. The higher grades of Sea Island and Egyptian long-fiber cottons are never used, mainly on account of the cost of the raw material. Tissue paper which finds extensive use with the celluloid manufacturers and producers of fine pyroxylin lacquers has previously been mentioned. The skeins of long stapled yarn used by von Lenk were undoubtedly of high purity and unusually free from waxy matters and inorganic constituents. At the same time, however, the fact that the skein condition was maintained throughout the entire nitration and purification process made it much more difficult and tedious to free the nitrocotton from the subsidiary products of the nitration process. The reduction of the cotton fibers to extremely short lengths in the pulping treatment removes in a great measure this difficulty.

Ordinary cotton waste is the principal form of cellulose used in the United States at the present time to produce the cellulose nitrates of industrial importance as distinguished from the higher nitrates used for explosives and as propulsive agents. This waste as obtained from the mills is in a very impure state, but so great has the consumption of this form of cotton become, that a separate industry has sprung up for the purpose of converting this mill waste into a form and purity suitable for nitration. The processes to which it is subjected are: degreasing by means of extraction with solvents, usually benzine or carbon tetrachloride; scouring, bleaching, and washing.

The effect of these treatments, when properly carried out, is to produce a fairly pure and resistant short-fiber cellulose, and these processes have now reached such a high state of perfection that it is not unusual to procure cottons of an ether-extract of not over 0.2%, and practically free from hydro- and oxy-cellulose. Cellulose nitrates of as high degree of purity as regards application of the heat test are not required for the production of photographic films and lacquers, and a mixed cotton waste can be used. The chief disadvantage of containing bits of wood, rubber, and other foreign bodies, is being overcome by improved methods of mechanical separation of these impurities[1] the presence of which, no doubt, are important sources of decreased stability.

The fact that cotton waste is plentiful, easily procured and reasonably cheap, can be depended upon to produce a nitrate satisfactory as regards nitrogen content, and solubility, gives it preference over other sources of cellulose. Some have claimed that cotton produced in a cold, wet season, in which the growth has been slow, as indicated by the thickened cellular wall and smaller canal, does not nitrate or neutralize as readily as a cotton grown in a favorable locality as regards humidity and high temperature, where the microscopic examination shows a thin-walled tube with a larger lumen. However, in practice no variation in the nitrating process is made as the result of the microscopical structure of the individual cotton fiber. Cotton waste has been used since the early days of guncotton manufacture.

In regard to the structure of the cellulose fiber as influencing ease of nitration, F. Nettlefold[2] says "it will be readily understood that the thin side-wall tubes of the cotton fibers are readily penetrated by the mixed acid, as compared with flax or other hard-walled fibers. In the latter, the walls are comparatively thick, and the central canal small," and the fact noted that flax is more difficult of nitration and subsequent neutralization is un-

---

[1] So-called weaving-mill waste is a material composed entirely of woven cotton fabric, often pieces of underwear and stockings, partly broken down by mechanical means. It differs materially in character, and as obtained contains starched and unstarched pieces. It is also apt to be overbleached and contain an undue amount of altered cellulose. In its best form it is a pure cotton cellulose and makes excellent pyroxylin, especially as regards yield, the large pieces retaining perfectly their shape during the nitrating process. It is at present difficultly procurable, and its cost is higher than the normal price of cotton waste. The short fiber from the cotton seed or the "combings" from cotton thread spinning and twisting, would no doubt make excellent material, if it could readily be obtained free from dust and particles of the seed husk. As it appears difficult to entirely remove the husk by mechanical means without subjecting to drastic chemical treatment, it is not used to any considerable extent.

[2] Chem. News, 1887, **55**, 306; abst. Proc. U. S. Naval Inst. 1888, **14**, 162; J. C. S. 1887, **52**, 792; Tech. Chem. Jahr. 1887–1888, **10**, 187; Ber. 1887, **20**, R, 676; Chem. Tech. Rep. 1887, **26**, I, 227; Jahr. Chem. 1887, **40**, 2273; Wag. Jahr. 1887, **33**, 569. G. Wolfram (Dingl. Poly. 1878, **230**, 45; abst. Chem. Centr. 1878, **49**, I, 403; Wag. Jahr. 1878, **24**, 449; Jahr. rein Chem. 1878, **6**, 478; Zts. Chem. Grossgew. 1878, **3**, 860) finds that concentrated acids give with cellulose from various sources the same final product, but with dilute acids, nitrating under the same conditions, cotton is the most readily attacked, then hemp, paper, straw and linen.

doubtedly due to the variation in microscopical structure. New Zealand flax gives the most perfectly fluid nitrates of any of the flaxes, it is claimed. It is therefore evident, that a given fiber requires an adaptation of the nitrating method to accord with the structure of its filaments, and in the most compact cells, as in certain evergreen trees, the ligneous fibers are very difficult of penetration.

G. Lunge,[1] who has examined the subject experimentally, "procured from the leading cotton mills in Switzerland authentic samples of the most varying grades of cotton, which were carefully cleaned mechanically and washed in the same way as in the manufacture of guncotton and nitrated with the same acid mixture (63.84 sulfuric, 16.96 nitric acid, 19.20 water), keeping all the conditions of the experiments exactly alike. Together he nitrated a sample of "chemically pure cotton wool," with the following results:

No.	Commercial Designation	Nitrogen %	Solubility in Ether-Alcohol %	Yield %
1	Chemically pure surgical cotton wool........................	11.76	100	159
2	American cotton "middling fair".	11.56	100	157
3	American cotton "Florida"......	11.67	100	153
4	Egyptian cotton, white, "Abassi"	11.69	100	155
5	Egyptian cotton, natural yellow..	11.61	100	154

"This shows that there is no essential difference in the quality of the colloidal cotton obtained from these extremely differing grades of cotton. They are all completely soluble; the nitrogen differs only by 0.13% among all the commercial cottons, and only by 0.20 in maxima against the pure surgical cotton. The latter is easily explained by the difference in purity, the surgical cottons containing only 0.05% ash, the commercial cottons averaging 0.5% ash.

Notwithstanding the above, it is the practical experience of manufacturers covering a number of years, and in which several hundred pounds of collodion nitrocotton was daily produced, that there is a great difference in the facility with which various kinds

---

[1] J. A. C. S. 1901, **23**, 578; abst. J. S. C. I. 1901, **20**, 1021; Chem. Centr. 1901, **72**, II, 34, 92, 764. See also Chem. Centr. 1899, **70**, I, 1272.

of cotton can be nitrated, and the ease with which the acid may be removed after nitration. The tendency to "burn" or fume in the nitrating bath, and toughness of cotton after nitration, are properties apparently sufficiently inherent in the cotton itself to differentiate one grade of cotton from another.

In the judgment of E. Piest,[1] for the manufacture of highly nitrated nitrocellulose, the material most largely employed is a mixture of spinning waste and American "linter-waste." The threads are first torn up and the lint passed through a cleaning machine to remove all mechanical impurities. Oil, natural wax, proteins, etc., are then removed by digesting with about 1% caustic soda solution under 3 atmos. pressure. The material must be tightly packed in the boilers and good circulation ensured; high purity of the soda and the exclusion of air during boiling and washing are advantageous. Bleaching must be very carefully controlled to preserve the chemical integrity of the cellulose; a little acetic acid may be added. The "copper value" (Schwalbe's test) must not exceed 1.0; fat and waxy matters, extracted by absolute alcohol, 0.5%; wood-gum, 2%. Tissue paper, from sulfite wood-pulp, may also be used for nitrating but is dearer than cotton-waste and yields an inferior product. For celluloid, great mechanical purity is required to avoid specks in the product; a low "copper value," not above 1.0 is specified. For collodion cotton, long, fine fibers and freedom from metallic impurities are required. For nitro-artificial silk, resin and oil are most objectionable impurities; as highly concentrated solutions of low viscosity are employed, the degree of bleaching, as indicated by the "copper value," may be higher. Wood celluloses give a softer but weaker silk; they should be purified by boiling under pressure with dilute sodium carbonate solution with the addition of a little caustic soda or sodium sulfide. For leather-substitutes the requirements are the same as for celluloid, but a higher degree of bleaching may be permitted. For cellulose acetate, freedom from knots is an additional requirement. For cuprammonium silk also, the cotton must be free from knots and the "copper value" must not exceed 1.0. According to one process, the cotton is bleached, then mercerized, washed, centrifuged and dissolved

---

[1] Papierfabr. 1914, **12**, 860; abst. C. A. 1914, **8**, 3362; J. S. C. I. 1914, **33**, 856; Zts. ang. Chem. 1914, **27**, II, 663.

without drying. For viscose, only wood cellulose is employed, generally purified by steeping in 2% hydrofluoric acid and then boiling out with 1% caustic soda; the "copper value" should not exceed 4.0.

According to R. S. Schwarz,[1] for use in the manufacture of nitrocellulose the waste from textile factories and cotton and linen rags are purified by boiling with dilute alkali under pressure, followed by mechanical treatment to remove knots, impurities, etc. bleaching with calcium hypochlorite, and disintegration in two machines. The loss in these operations varies according to the kind of rags from about 20% to 40%. To prevent loss in the form of dust attempts have been made to cut the rags into fragments before bleaching, but this caused irregular nitration. The following specifications have been issued: Maximum ash in nitration cotton wool, 0.6% (or 1.2% in the torn partially purified rag material); fat, 0.4% (or 1.0% in the impure material); and water, 6%. A white color, freedom from chlorine, acidity, and dust, and the absence of vegetable impurities are also specified. Too high ash results in waste of the nitrating acids, and causes difficulty in gelatinizing the nitrocellulose powder, while fat in excess of the specified amount increases the difficulty of nitration and leads to overheating of the mixture. Short fiber fragments are unsuitable for nitration, since some of the nitrocellulose then remains dissolved in the waste nitrating acid, and causes explosions when this is redistilled.

Preparation of Cotton for Nitration. As has previously been mentioned, the celluloses of commerce in their natural state are not in a favorable condition for the manufacture of cellulose nitrates, being usually mixtures composed partly of cellulose of varying degrees of purity and freedom from incrusting matter and partly of various kinds of conglomerates closely adhering thereto. The chemical purity of cellulose to be nitrated is of the utmost importance in the manufacture of a pure cellulose nitrate, the uniformity of the action of the nitrating agents (nitric and sulfuric acids) and the thoroughness of the washing by which these acids are subsequently removed from the nitrated product depends in a great measure upon the uniformity or completeness

---

[1] Oesterr. Chem. Ztg. 1919, **22**, 50, 57; abst. J. S. C. I. 1919, **38**, 602-A.

of the mechanical condition or division of the cellulose employed for esterification. Many attempts which have been made to bring the cellulose of commerce into the condition in which it is free from the defects above mentioned have failed, partly because the material manufactured was not perfectly free from incrusting bodies, and also to the fact that the fat and other extraneous matter had not been completely removed from the cotton filament.

In the later and well known process of J. Lewin[1] the cotton by successive treatment with alkali and acids is freed from the usually occurring impurities, then reduced to a fine powder by means of a reducing cylinder, after which it is submitted to the action of steam at high pressure until reaction takes place, the operation being arrested when a gelatinous mass is obtained which can be preserved indefinitely from change by storage under water. Cellulose prepared in this manner is especially applicable for nitration purposes where a cellulose nitrate is to be combined with nitroglycerol, for the gelatinous mass, even if incompletely nitrated, appears to go into a homogenous plastic mass when incorporated with nitroglycerol.

J. Daniel and F. Benoist[2] first boil the cellulose in an autoclave with circulation device and under one to four atmos. pressure with a mixture of 2% caustic soda, 1% sodium carbonate, 1% sodium sulfate, and 1% of ethylene trichloride. After this combined saponification and extraction has been carried on for 4 to 12 hours, the cotton is rinsed with ordinary water, washed with soap, bleached with hypochlorite and then dried. It is claimed cotton prepared in this way is especially suitable for nitration of the finer grades of nitrocellulose, specifically those intended for the manufacture of continuous photographic film, and thermoplastic nitrocelluloses.

J. Foltzer[3] first boils 100 kilos of cotton in 1000 liters of a solution containing 30 kilos of sodium carbonate and 50 kilos of sodium hydroxide. The solution is placed in a hermetically sealed reservoir, heated to 110°-120° under a pressure of $^1/_2$ atmosphere continuously during a four-hour period.

In order to remove the fat, wax and resinous matter from

---

[1] E. P. 4943, 1880; abst. Chem. Ind. 1882, **4**, 65, 180.

[2] F. P. 465471, 1913; abst. J. S. C. I. 1914, **33**, 588; 1916, **35**, 597; Mon. Sci. 1916, **83**, 12; Chem. Ztg. Rep. 1914, **38**, 582.

[3] F. P. 345687, 1904; abst. J. S. C. I. 1905, **24**, 85; Zts. ang. Chem. 1905, **18**, 434; Mon. Sci. 1906, **65**, 36; 1907, **67**, 603.

cotton and similar fibers, P. Girard[1] treats with solvents as methyl, ethyl or amyl alcohols, acetone, carbon tetrachloride, trichloroethane, or the chlorine derivatives of ethylene and ethane, either alone or in mixture to which may be added from 5% to 10% of a solution of aqueous commercial formaldehyde. The cost of the solvents renders this method unduly expensive.

In the process carried out by J. France,[2] cotton or other fiber, preferably in its natural state, but also in the state of roving or loose twisting, is ground or cut into short lengths so as to form virtually a powder, in which condition it is subject to the action of the nitrating acids, applied in the usual proportions for producing either the soluble or insoluble kinds of cellulose, and after being well washed with water so as to remove these residues is ready to use in the form of a pulp or may be dried and utilized in the condition of a powder. This process, which was designed to increase the stability of the resulting nitrocellulose, failed in that the yields obtained were too low due to the large amount of cotton being obtained in the nitrating acids in suspension and in solution.

In the process of O. Röhn,[3] the treatment of raw cotton with boiling alkalis preparatory to bleaching is omitted and the material is softened by steeping in 0.1% aqueous solution of pancreatin at 20°–40° for some hours and then bleached with the usual agents. Other enzymes such as papayotin, or ricinus enzymes may be used or fresh organs or preparations instead of the commercial enzyme. It will be observed that the essence of this invention consists in the attempt to emulsify fatty materials by means of an amylolytic enzyme.

E. Berl[4] proposes to depolymerize the cellulose molecule by heating the cotton in an inert gas, claiming that nitrocellulose prepared from cellulose depolymerized in this manner is better in that it gives more fluid solutions and a higher stability and

---

[1] F. P. 443897, 1912; abst. Kunst. 1912, **2**, 456; J. S. C. I. 1912, **31**, 1120; J. Soc. Dyers, 1912, **28**, 310.

[2] U. S. P. 420445, 1890. E. P. 5364, 1890; abst. J. S. C. I. 1890, **9**, 821.

[3] E. P. 100224, 1916; abst. J. S. C. I. 1916, **35**, 1057; J. S. C. I. Ann. Rep. 1917, **2**, 127. D. R. P. 297324, 1915; abst. J. S. C. I. 1917, **36**, 869; Chem. Zentr. 1917, **88**, I, 983; Chem. Ztg. Rep. 1917, **41**, 148.

[4] D. R. P. 199885, 1907; abst. Mon. Sci. 1911, (5), 74, 93; Zts. ang. Chem. 1908, **21**, 2233; Chem. Zentr. 1908, **79**, II, 466. Chem. Ztg. Repert. 1908, **32**, 382; Chem. Ind. 1908, **31**, 454; J. S. C. I. 1908, **27**, 937; Wag. Jahr. 1908, **54**, II, 355. Aust. P. 37030, 1908.

capacity for gelatinization than nitrocellulose made from ordinary cotton.

I. Kitsee[1] has described a method for obtaining cotton "fly" or linters in a manner so that it is especially adaptable for subsequent nitration. H. de Chardonnet[2] prefers to heat during 6 to 8 hours continuously at a constant temperature, from 150° to 170° the cellulose material in a stove having shelves, which are gratings of tubes for circulation of steam at a pressure of 8 to 10 atmospheres. Suitable valves serve to regulate the air circulation so as to determine the desired temperature. The cellulose when the operation is ended, is immersed still warm in the nitrating bath. Nitrocellulose prepared from cotton treated in the above described manner gives a very low viscosity and thin solutions which are especially applicable to the formation of nitrocellulose artificial filaments and aeroplane lacquers.

C. Waite and J. Hedin[3] have described a process whereby a raw material containing cellulose is digested with caustic soda which has been treated with a small quantity of sulfur so that the amount of sodium sulfide present is less than 0.5%. This small quantity of sulfide, according to the patentees, is sufficient to neutralize the effect of the formed oxygen present, and thus prevent or at least retard the formation of oxycellulose, while on the other hand it is insufficient to exert an appreciable digesting action.

In the C. Kellner process,[4] cellulose which is to be purified is treated with water or preferably with milk of lime or a very weak solution of an alkaline carbonate or hydroxide and after the excess of liquid has been removed by means of a hydro-extractor or otherwise, as, for example, by pressing, the cellulose under treatment is subjected to the action of chlorine gas derived

---

[1] U. S. P. 789978, 1905; abst. J. S. C. I. 1905, **24**, 686. D. R. P. 188077; abst. Wag. Jahr. 1907, II, 498; Chem. Zentr. 1907, **78**, II, 1879; Zts. ang. Chem. 1908, **21**, 269.

[2] E. P. 19560, 1891; abst. J. S. C. I. 1892, **11**, 939; J. Soc. Dyers, 1892, **8**, 19. D. R. P. 64031, 1891; abst. Mon. Sci. 1893, **42**, 15, 16; Ber. 1892, **25**, 892; Chem. Centr. 1892, **63**, II, 1088; Wag. Jahr. 1892, **38**, 376; Zts. ang. Chem. 1892, **5**, 499.

[3] U. S. P. 1212158, 1917; abst. J. S. C. I. 1917, **36**, 288; C. A. 1917, **11**, 705.

[4] E. P. 24542, 1902. Fr. P. 326313, 1902; abst. J. S. C. I. 1903, 817, 1145; Mon. Sci. 1904, **61**, 46; Chem. Ztg. 1903, **27**, 902. See also C. Kellner, E. P. 5420, 1890; abst. J. S. C. I. 1891, **10**, 62.

from the electrolysis of a metallic chloride.

O. Schmidt[1] prefers to reduce the cellulose to a firm granular condition which is accomplished by treatment, for instance, by means of churn-shaped pounding mills (in order to effect the separation of any cells which may adhere mechanically) and thereupon it is passed in the wet state through a grinding process, for instance, in edge runner mills. The moist plastic mass obtained is then granulated by passing through sieves and the grains rounded off, for instance, by the aid of polishing casks, whereupon they are dried, the resulting granulated material being firm and horn-like. The cellulose thus reduced to the granulated condition is then changed into nitrocellulose in the usual manner.

In the method as devized by C. Budde and the Hendon Paper Works Co.,[2] cellulose is saturated with free chlorine or bromine prior to nitration, the process being alleged as particularly applicable to wood, esparto or straw cellulose, or impure or degenerated cotton. Cellulose when made by the method devised by H. Arledter[3] is treated in an apparatus[4] in the presence of aluminium sulfate or of alums or of sulfate or sulfite of zinc or of compounds known to have a parchmentizing effect and are either subjected to an alternative vacuation and admission of air which may be ozonized, or a peroxide of hydrogen or other oxidizing agents. This treatment results in the hydrolysis of the cellulose and the formation of a more or less jelly-like material which can be used as a base for the manufacture of nitrocellulose explosive. H. Landell[5] purifies cotton waste for making cellulose by treating waste successively with boiling 5% caustic soda solution for 10 hours, washing, treating with a 4° Tw. calcium hypochlorite solution, again washing, shredding and finally drying. The process of E. Nowicki[6] is similar. According to A. Hertzog,[7] the prepar-

---

[1] E. P. 116, 1904; abst. J. S. C. I. 1904, **23**, 385; Chem. Ztg. 1905, **29**, 514.

[2] E. P. 10292, 1915; abst. C. A. 1917, **11**, 100; J. S. C. I. 1916, **35**, 656; Kunst. 1917, **7**, 114.

[3] E. P. 16085, 1912; 684, 1913; abst J. S. C. I. 1913, **32**, 865; C. A. 1914, **8**, 247.

[4] Similar to that described in E. P. 2018, 1910; abst. C. A. 1910, **5**, 2947; J. S. C. I. 1911, **30**, 205. F. P. 418584; abst. J. S. C. I. 1911, **30**, 80.

[5] U. S. P. 1222422, 1917; abst. C. A. 1917, **11**, 1904; J. S. C. I. 1917 **36**, 544.

[6] F. P. 402197, 1909; abst. J. S. C. I. 1909, **28**, 1274.

[7] Centr. f. d. Textil Indus. 1890, **21**, 975; abst. J. S. C. I. 1891, **10**, 161; Chem. Tech. Rep. 1890, **29**, II, 143; Chem. Ztg. Rep. 1890, **14**, 355.

ation of cotton waste for the manufacture of smokeless powder has been brought to a high state of perfection in England, due to the fact that a large amount of cotton waste is the natural result of the spinning and weaving processes used there.

In Germany, according to M. Gladbach,[1] in order to meet the requirements of the military authorities for purified cotton suitable for smokeless powder manufacture, the cotton must sink in water, within two minutes, when nitrated must not become brown must yield not over 0.9% material soluble in ether and the cotton must be free from chlorine, lime, magnesium, iron or sulfuric or phosphoric acid compounds. Cotton wool or waste to fulfill the above requirements may be purified in the following manner: first, boiling the cotton in caustic soda solution under pressure, washing, then bleaching, washing again, treating with sulfuric or hydrochloric acids, washing again, then centrifugalizing and finally drying. Waste cotton containing fat may be preferably treated in the following manner. First boil in lime water under pressure, then wash, after which the product is boiled in a caustic soda solution under pressure, then wash, bleached with chlorine, washed again, acidified and finally centrifugalized and dried. In very impure waste the boiling process in lime water requires a longer period of time but the caustic soda boil should not be prolonged. The boiling process may more preferably be carried out in an autoclave of the system supplied by Schenrei-Roth. For the drying, M. Gladbach recommends the employment of a Zittaeur machine, claiming the washing may more preferably be done by means of a Mather-Platt bleaching apparatus. When purifying cotton waste by the above process the following are the losses on a commercial scale:

Transportation and packing	2 to 5%
Boiling first and washing	5 to 40%
Bleaching with chlorine	15 to 20%

In the process as practiced in Austria, the purification of raw cotton from seed and other matters foreign to cellulose constitutes a most important preliminary operation for the formation of cellulose for military and peaceful purposes. The cotton waste now used in making guncotton it is stated, has undergone so thorough a purification of the various manufacturing processes through which it has passed that while no further preliminary purification

---

[1] Chem. Ztg. Rep. 1890, **14**, 354.

is required, the finished guncotton as obtained from it is practically pure nitrocellulose of high stability.

J. Hall[1] has patented a process for artificially maturing cotton, the fibers of which have greater tensile strength and a greater percentage of cellulose than the fibers of naturally matured cotton, and this is obtained by artificially maturing cotton bolls, after dusting them with a mixture containing starch 50 and talcum 25 parts.

The process for preparing artificial cotton as elaborated by J. Bourbon and P. Cassier[2] consists in pouring the viscose preparation of cellulose into a rotating centrifugal of the same type as it used for obtaining sugar in the form of fine threads ("sucre fils"). This apparatus throws the cellulose out of the cage into the surrounding vessel where it collects in the form of a very fine loose cotton, which can be spun in the ordinary way or used for nitrating by merely drying.

In the preparation of fleece from wood pulp suitable for nitration, the dry fibrous material is projected by air blast against beating arms which open and clean the fibers, whence it is then driven upwards by an air blast through the beating chamber against moving sieve surfaces. It is then conveyed by suction in the usual manner to form a firm fleece.[3]

A. de Salas[4] prepares flock cotton for the manufacture of nitrocellulose by soaking rags in a solution of soap and an alkali, washing and drying, and then mechanically comminuting the cotton to a flocculent condition. H. Nishida[5] has compared loose cotton of various kinds, mercerized cotton yarn, and tissue papers prepared from other cellulosic materials as raw material for the manufacture of celluloid. From the results obtained the various raw materials are classified as follows as to their suitability: (1) Unbleached mercerized cotton; tissue paper from white rags and cotton fishing nets. (2) Bleached mercerized cotton; tissue

---

[1] U. S. P. 1201288, 1916; abst. C. A. 1916, **10**, 3167; Kunst. 1917, **7**, 83.

[2] F. P. 429679, 1911; abst. J. S. C. I. 1911, **30**, 1297; Kunst. 1911, **1**, 456; J. Soc. Dyers, 1911, **27**, 224.

[3] D. R. P. 294079, 1915; abst. C. A. 1918, **12**, 868; Chem. Ztg. Rep. 1916, **40**, 400.

[4] U. S. P. 1249726; abst. C. A. 1918, **12**, 428.

[5] Jour. Ind. Eng. Chem. 1916, **8**, 1096; abst. J. S. C. I. 1917, **26**, 27. Paper, **19**, No. 17, p. 13; C. A. 1917, **11**, 209; Ann. Rep. Soc. Chem. Ind. 1917, **2**, 137.

from colored rags; tissue from linen fibers. (3) Papers from bast fibers; weavers waste cotton yarn, scoured and bleached. (4) Bamboo tissues as free from adulteration as possible, and wet beaten. (5) Chemical wood fiber and straw, as free from knots as possible. (6) Mechanical wood fiber mixed with a little cotton.

In the method of T. Nordenfelt and V. Meurling,[1] vegetable fiber is treated with hydrochloric acid, either in the liquid or gaseous form, and dried, when it is then in a condition, according to the patentees, for easy nitration. The process of Liedbeck[2] is somewhat similar and results in the formation of very finely divided cellulose. Readily soluble derivatives upon esterification, may, according to O. Glum & Co.,[3] by treating the cotton with glycerol at temperatures above 100° C. Drying the cellulose in an oil bath at 140° C. for 4 hours, and then proceeding with the nitration in the usual manner. By the preliminary treatment of the cotton in this manner, the patentees claim to be able to produce cellulose esters which require much less solvent for solution, and of lower viscosity, without at the same time interfering in any way with the desirable qualities of the ester.

The "cellulose substitute" of O. Mueller[4] is prepared by boiling cotton-seed hulls in 3% NaOH solution, washed with water, treated with 0.1% potassium permanganate solution, heated to 40° in a solution containing 0.6% HCl and sodium acid sulfite, and bleached with chlorine.[5] The method of preparing cotton

---

[1] E. P. 6515, 1884.

[2] D. R. P. 96109, 1897; abst. Chem. Centr. 1898, **69**, I, 1222; Mon. Sci. 1898, **52**, 178; Jahr. Chem. 1898, **51**, 1382; Wag. Jahr. 1898, **44**, 372; Zts. ang. Chem. 1898, **11**, 167.

[3] Belg. P. 211385, 1908. D. R. P. 217316, 1910; abst. J. S. C. I. 1910, **29**, 417; Wag. Jahr. 1910, **56**, II, 433; Zts. ang. Chem. 1910, **23**, 526; Chem. Centr. 1910, **81**, I, 490; Chem. Ztg. Rep. 1910, **34**, 47; Chem. Ind. 1910, **33**, 59; Chem. Zts. 1910, **9**, No. 1670. E. Berl (D. R. P. 199885, 1907; abst. Chem. Zentr. 1908, **79**, II, 466; J. S. C. I. 1908, **27**, 937; Mon. Sci. 1911, **74**, 93; 1916, **83**, 80; Chem. Ind. 1908, **31**, 454; Chem. Ztg. Rep. 1908, **32**, 382; Wag. Jahr. 1908, **54**, II, 355; Zts. ang. Chem. 1908, **21**, 2233) first removes the water from cellulose, then is heated at a temperature above 100° C. in the presence of inert gases (N_2, CO_2, water gas, coal fire gas, or superheated steam, thus apparently inducing polymerization of the cellulose.

[4] U. S. P. 930874, 1909; abst. C. A. 1909, **3**, 2627; J. S. C. I. 1909, **28**, 1001. E. P. 3211, 1906; abst. J. S. C. I. 1906, **25**, 865. See O. Mueller, U. S. P. 931634, 1909. Mon. Sci. 1910, **73**, 94.

[5] Neutralization of the sodium hydroxide extract yields a precipitate said to be useful as a varnish gum or lac substitute.

for nitrating as patented by the Zellstoff-Fabrik Waldhof[1] is similar to those already described.

A recent invention has been published[2] which describes the treatment of cellulose with free chlorine or bromine before nitration, to enhance its value.

The Dynamit A. G. Nobel[3] have described a method of treatment of cellulose before nitration with sulfuric acid or zinc chloride, in order to impart desirable properties to the cellulose. They first treat cotton with 5% H_2SO_4 at 100°, wash until neutral, and then dry, after which the usual nitration process is carried on. After the sulfuric acid treatment, the cellulose may readily be reduced to a structureless powder.

The Utilization of Short Fibers. In the earlier formative

---

[1] D. R. P. 64878; Mon Sci. 1893, **42**, 208; Ber. 1893, **26**, 78; Wag. Jahr. 1892, **38**, 371; Zts. ang. Chem. 1892, **5**, 706. C. Budde and Hendon Paper Works, E. P. 10292, 1915; abst. C. A. 1917, **11**, 100; J. S. C. I. 1916, **35**, 656; Kunst. 1917, **7**, 114. The main advantages claimed for this process are that secondary reactions during nitration do not occur to anything like the same extent as in the case when the treatment with free chlorine or bromine is omitted, this fact being most strikingly observed when the nitration takes place under partial vacuum, in which case esparto cellulose develops a continual current of gases. If the same cellulose has been previously treated with chlorine or bromine, hardly any gas is said to occur. It is also alleged that the tendency toward rise in temperature during nitration is materially diminished, and the final nitrated product instead of being yellow or brown, is of a pure white color. The stability of the nitrated product is also said to be increased.

[2] D. R. P. 4410, 1878; abst. Chem. Centr. 1879, **50**, 720. See also: E. Fremy and V. Urbain, D. R. P. 22370, 1882; abst. J. S. C. I. 1883, **2**, 276; Dingl. Poly. J. 1883, **248**, 472; Wag. Jahr. 1883, **29**, 1036; Chem. Ind. 1883, **6**, 135; Mon. Sci. 1884, **26**, 27. G. Bentley, E. P. 2262, 1874. C. Chevalier and A. Lejeune, Bull. assoc. instit. Meurice, **1**, 250; abst. Bull. Soc. Chim. Belg. **27**, 99; C. A. 1913, **7**, 2312. H. Dutschke, F. P. 467670, 1914. E. P. 2164, 1914; abst. J. S. C. I. 1914, **33**, 860; C. A. 1915, **9**, 1997. M. Henry, E. P. 1454, 1860. R. Hollins and T. Taylor, E. P. 23192, 1908; abst. J. S. C. I. 1909, **28**, 1270; C. A. 1910, **4**, 1544; J. Soc. Dyers, 1910, **26**, 13. J. Ketcheson, F. P. 407616, 1909; abst. J. S. C. I. 1910, **29**, 559. E. P. 22111, 1909; abst. J. S. C. I. 1910, **29**, 875; Chem. Ztg. Rep. 1911, **35**, 112; Kunst. 1911, **1**, 34; U. S. P. 987629, 1911; abst. C. A. 1911, **5**, 2003. G. MacDonald, Arms and Explosives, 1909, **17**, 23; abst. C. A. 1909, **3**, 1459. J. Mewburn, E. P. 7187, 1885; abst. J. S. C. I. 1886, **5**, 322; J. Soc. Dyers, 1886, **2**, 110. A. Müntzing, F. P. 376894, 1907. U. S. P. 882790, 1908; abst. J. S. C. I. 1907, **26**, 1027; 1908, **27**, 418; C. A. 1908, **2**, 2300. C. Piest, Der Papier Fabrikant, 1914, 78; abst. Kunst. 1914, **4**, 293. O. Silberrad, E. P. 28193, 1910. F. P. 434709, 1910; abst. J. S. C. I. 1912, **31**, 67; C. A. 1912, **6**, 1534; J. Soc. Dyers, 1912, **28**, 85; Mon. Sci. 1912, **77**, 569; 1913, **79**, 181; Chem. Ztg. Rep. 1912, **36**, 273.

[3] D. R. P. 4410, 1878; abst. Chem. Tech. Mitth. 1878–1879, **28**, 295; Zts. Chem. Grossgew. 1879, **4**, 287; Dingl. Poly. 1879, **232**, 188; Deutsche Ind. Ztg. 1879, 170; Ber. 1879, **12**, 712; Chem. Ztg. 1879, **3**, 197; Wag. Jahr. 1879, **25**, 419; Chem. Ind. 1879, **2**, 171; Chem. Tech. Rep. 1879, I, 287; J. A. C. S. 1879, **1**, 303.

days of the cellulose nitrate art, it was the common practice, in order to maintain a high yield, to employ the higher priced long-staple cotton in nitrating processes, but with the development, refinement and ramifications of the art, competition became so keen as to necessitate the employment of the cheaper short staple varieties of cotton for this purpose; for instance, W. Crum,[1] in his investigations upon the nitrogen content of nitrocellulose employed fine Sea Island cotton, carded, bleached, purified by boiling with caustic soda and a final treatment with dilute nitric acid. The cotton so employed lost 5.5% of its weight containing but 0.09% ash.

A Grandjean[2] developed a new product termed by him "snow paper" or "snow pulp," and produced by disintegrating paper containing no size, which was afterwards rolled and made into sheets and either in the loose or compressed form employed for nitrating purposes, specifically for the manufacture of collodion and celluloid. The artificial cotton wool patented by A. Bloch[3] is prepared by first washing cellulose with alkali to free it from fatty matters, then bleached in a solution composed of 10 kilos of calcium hypochlorite, 6 kilos of aluminium sulfate, 2 to 3 kilos of magnesium sulfate and 200 kilos of water. After washing and drying in a centrifugal extractor, cellulose is purified by solution in Schweizer's reagent, the solution filtered and then precipitated. To prevent the precipitated fibers from becoming agglomerated mechanical arrangements are specified.[4]

The Verein f. Chemische Industrie in Mainz[5] prefer to treat

[1] Phil. Mag. 1847, (3), **30**, 426; abst. J. prakt. Chem. 1847, **41**, 201; J. Pharm. 1847, (3), **12**, 296; Jahr. Chem. 1847–1848, **1**, 1130; Glasgow Phil. Soc. Proc. 1844–1848, **2**, 163; Ann. 1847, **62**, 233.

[2] E. P. 22566, 1894; abst. J. S. C. I. 1896, **15**, 132. See W. Ragsdale, E. P. 10182, 1906. Also E. P. 8591, 1891; 15164, 1893; 10183, 1906.

[3] F. P. 447068, 1911; abst. J. S. C. I. 1913, **32**, 283; Kunst. 1913, **3**, 74. I. Kitsee (U. S. P. 789977, 1905; abst. J. S. C. I. 1905, **24** 686) prefers to nitrate the cotton seed with its adherent fiber, the nitrated product being then treated with a solvent which dissolves the nitrocellulose. The solution is then separated from the residue of the seed. The author, in trying this method, found "fume offs" very liable to occur. The Rheinische Kunstseidefab. (D. R. P. 208675, 1909; abst. Chem. Zentr. 1909, **80**, I, 1444; Chem. Ztg. Rep. 1909, **33**, 216; Wag. Jahr. 1909, **55**, II, 508; Zts. ang. Chem. 1909, **22**, 942) purify linters by boiling with alkali or alkaline permanganate, followed by a light bleaching with chlorine.

[4] Bloch, Belg. P. Appl. Aug. 18, 1911.

[5] D. R. P. 290131, 1913; abst. J. S. C. I. 1916, **35**, 533; C. A. 1916, **10**, 2803. See also Poly. Centr. 1866, **32**, 75; Chem. Zentr. 1916, **87**, I, 352; Chem. Ztg. Rep. 1916, **40**, 96; Zts. ang. Chem. 1916, **29**, 144.

cotton with a small quantity of acid or acid salts. e. g., 0.01–0.02 sulfuric acid, subsequently drying at a low temperature. By this treatment the patentees claim the strength of the cotton is increased by 10% to 30% and not more than traces of oxy- or hydro-cellulose are formed. The cotton so treated is claimed to behave like mercerized cotton in giving viscose solution of improved solubility and to be especially applicable for the nitration of cotton where solutions of great fluidity are desired.

In the use of short staple cotton, specifically linters, G. Mowbray[1] apparently was the first to recognize the commercial advantages accruing from the use of short fiber cotton as linters. In the process as disclosed in the application of T. Newsome,[2] the short cotton fibers which remain attached to the seed hulls after the fibers fit for spinning have been taken away, are, as the patentee has pointed out, difficult of utilization due to the tenacity with which the brown fragments of hull adhere to the cotton filaments. The carded cotton fiber containing waxy constituents of an unusually resistant nature and insoluble in water are extracted by means of volatile hydrocarbons, such as petroleum naphthas to remove these waxes as well as other incrustated matters of the hull without injury to the fiber.

To attain this end the inventor treats the seed hulls and the attached fibers with the vapors of boiling naphtha, the vapors entering at the top of the extraction vessel, condensing and flowing down through the mass, the solvent containing the dissolved matters being passed back into the evaporator. After the soluble matters have all been extracted in this manner, the naphtha

---

1. E. P. 20978, 1890; abst. J. S. C. I. 1891, **10**, 271. D. R. P. 60595; abst. Wag. Jahr. 1891, **37**, 431; Ber. 1892, **25**, 352; Mon. Sci. 1892, **40**, 172; 1893, **42**, 861.

2. U. S. P. 683785, 1901; abst. J. S. C. I. 1902, **21**, 63; Papier Ztg. 1901, **24**, 3321; Mon. Sci. 1902, **58**, 16. E. P. 19585, 1901; abst. J. S. C. I. 1902, **21**, 788. R. Fabre (E. P. 10260, 1912; abst. C. A. 1913, **7**, 3546; J. S. C. I. 1913, **32**, 284) employs carbon tetrachloride and trichloroethylene for the same purpose. For the cotton waste cleansing apparatus of A. Poulson and W. Mate, see E. P. 110691, 1917; abst. J. S. C. I. 1918, **37**, 5-A. O. Guttmann described the use of cotton waste for nitrocellulose manufacture in 1883 (Dingl. Poly. 1883, **249**, 509). In the F. Stockton method of purification (U. S. P. 1295078, 1919; abst. J. S. C. I. 1919, **38**, 319-A. E. P. 132422 1919; abst. J. S. C. I. 1919, **38**, 745-A) cottonseed hull fiber is softened by boiling in a 4% solution of caustic soda for about 5 hours. The boiled fiber is placed between rollers in order to disintegrate the associated hull particles, and then subjected to a cleaning operation to separate the fine, disintegrated hull particles from the fibers.

adhering to the mass is driven off by hot water and the contents of the extraction vessel removed and boiled with alkali, preferably with a 2% solution of caustic soda, under a pressure of 50 lbs. per square inch, for four hours. By this treatment the residues of seed hulls are dissolved by the alkali and the fibers are then, after washing, in suitable condition for nitration. The method of F. and A. Van den Bosch and O. Müller[1] is similar.

The treatment of cotton seed hulls, as elaborated by C.

---

[1] E. P. 3214, 1906; abst. C. A. 1907, **1**, 658; J. S. C. I. 1906, **25**, 865; U. S. P. 930874; abst. J. S. C. I. 1909, **28**, 1001; C. A. 1909, **3**, 2627; Mon. Sci. 1910, **73**, 94. They boil the cotton seed husks including the non-fibrous portion, with caustic soda solution of 3°–10° Bé., according to the origin of the cotton seed and the composition of the material operated upon, either at atmospheric or increased pressure. The material after being washed free from alkali is next oxidized in a 0.1% potassium permanganate bath for 30 minutes at about 20° with stirring. From this bath, the mass without being washed is brought into a bath of sulfurous acid, the action being assisted by warming. When the cellulose has been transformed into a "transparent grissly mass," it is finally washed to neutrality and dried.

M. Wertz (E. P. 12422, 1910; abst. J. S. C. I. 1911, **30**, 798; J. Soc. Dyers Col. 1911, **27**, 214; Kunst. 1911, **1**, 295; Chem. Ztg. 1911, **35**, 520) uses for the preparation of artificial filaments and for nitrocellulose manufacture, fibers from the so-called "silk cotton family," obtaining best results from kapok (the fiber covering the sides of the tropical tree, *Eriodendron anfractuosum*), as well as the fiber obtained from the cotton free, *Bombax malabaricum*. The fiber from either of the above mentioned sources is first treated with alkali to remove fat and oleaginous matter, then bleached, when it may be directly dissolved, as in cuprammonia or zinc chloride. The patentee has found that by the use of the above fibers, artificial filaments can be manufactured of comparatively high counts.

P. Minck and Bremer Baumwollewerke (E. P. 12718, 1906) have devised an apparatus for separating in a purely mechanical manner and by means of a dry method, waste products containing fiber, especially cottonseed hulls either alone, or when mixed with cotton, linen or hemp waste. The loosening or opening processes to which they are subjected when working according to the directions laid down in the patent specification, are such that the fibrous constituents are obtained undamaged and not reduced in length more than is proper considering their intended industrial utilization for purposes of nitration.

G. Atkins (E. P. 7058, 1903; abst. J. S. C. I. 1904, **23**, 385; Chem. Ztg. 1904, **28**, 732; Mon. Sci. 1905, **62**, 68) has received patent protection for an invention which relates to the manufacture of nitrated cellulose from any suitable organic material of cellular origin, but more especially from the waste from cottonseed remaining after the oil has been expressed from the seed and the material suitable for making oilcake has been sifted out. This waste, which ordinarily consists of the husk of the seed with tufts of cotton still adhering thereto, is considered very suitable for nitrocellulose manufacture when submitted to the following treatment: The waste is first treated with an alkali, washed and then bleached in the usual manner. The patentee claims that a specially novel feature of his process is the bleaching with "chloride and oxychloride of soda," for "when nitrated material is to be used for the manufacture of celluloid it materially improves its color and consequently the market value of the product."

Cross,[1] involves the treatment of the hulls with an alkaline solution, preferably caustic soda, so as to obtain a dark colored liquor and a fibrous residue, the cellulose component portion being obtained in a pure form by boiling and washing and finally submitting to the action of chlorine gas in a suitable chamber until such constituents as will combine with the chlorine are saturated. The chlorinated product is then washed to remove acid constituents, next digested with boiling water or with an alkaline solution, preferably a mixture of sodium carbonate and sodium sulfite, in which the chlorinated products are soluble and is finally washed.

J. Cochran[2] has assigned to F. Taylor an invention consisting in the utilization of the fuzz of cotton seed hulls to produce a cellulose useful for the manufacture of guncotton and other explosives in which the cotton seed, after being divested of all staple fiber, such as cotton and lint, there still remains on the hull a long staple not of the order of fuzz which, by means of the patentee's process, is made commercially useful. In order to attain his object, the divested hull is subjected to attrition whereby the fuzz is disconnected from the hull proper and by an air blast or other means the fuzz is separated from the hull and collected by itself. In this manner the use of solvents is eliminated.

The method of L. Guiguet[3] is really an immaterial improvement upon the previously described process of P. Girard.[4]

M. Marsden[5] recovers fibers from waste portions of cotton plants by comminuting and mechanically separating the light and heavy portions by a blower or cyclone separator, treating with water and steam under pressure to extract the sugar, tannin, coloring matters, etc., and then treating with an alkaline solution,

---

[1] E. P. 8545, 1904; abst. J. S. C. I. 1905, **24**, 288. See also U. S. P. 807250, 1905; abst. Mon. Sci. 1907, **66**, 15; 1910, **73**, 160; J. S. C. I. 1906, **25**, 34; Chem. Zts. 1906, **5**, 63. E. P. 8544; abst. J. S. C. I. 1905, **24**, 340.

[2] U. S. P. 822430, 1906. Chem. Ztg. Rep. 1907, **31**, 91; Chem. Zts. 1906, **5**, 376; Zts. Schiess. Spreng. 1906, **1**, 364. E. P. 12920, 1906; abst. J. S. C. I. 1907, **26**, 775; C. A. 1907, **1**, 2512.

[3] F. P. 464028, 1913; abst. J. S. C. I. 1914, **33**, 376; C. A. 1914, **8**, 3122; Mon. Sci. 1916, **83**, 67; Chem. Ztg. Rep. 1914, **38**, 363.

[4] F. P. 438131, 1911; abst. Kunst. 1912, **2**, 437; J. Soc. Dyers Col. 1912, **28**, 200; Mon. Sci. 1913, **79**, 14.

[5] U. S. P. 1143587, 1915; abst. C. A. 1915, **9**, 2311. The J. Cochran method of obtaining the fuzz from cotton-seed hulls for use as cellulose in the manufacture of guncotton is described in E. P. 12920, 1906; C. A. 1907, **1**, 2512; J. S. C. I. 1907, **26**, 775.

also under pressure, to remove incrustating substances.

E. de Segundo has devized a machine applicable for this purpose.[1]

A process for separating the short cotton fibers from cotton seed after the bulk of the cotton has been removed, and now said to be employed on the continent, has been described by E. Drabble[2] in which the cotton is first of all mechanically removed from the seeds and is then "winnowed" and collected. After this it is subjected to chemical treatment to remove the impurities, and short fiber cotton thus prepared is said to have been used with great success not only in the manufacture of blotting paper, owing to its high absorptive value, but especially for the preparation of guncotton and other forms of nitrocellulose.

In the employment of linters and other short fiber cottons, the loss in the various mechanical treatments to which it is necessarily subjected as a preliminary to use for nitrating purposes is considerable. The following figures, based on the actual factory runs, are representative of these various losses:

Shipper's weight, gross	36,294 lbs.
Tare	556 lbs.
Net weight paid for	35,738 lbs.

The tare comprised wire bale 143 lbs., paper and string, 413 lbs., total, 556 lbs. The moisture in the cotton 5.19%, giving a net weight of dry cotton of 33,880 lbs. The waste of cotton at the picking house was 86 lbs., at the drying house 91 lbs., in the weighing room 50 lbs., a total of 227 lbs. 1173 wringers were dipped, none of which fired, employing 148,920 lbs. of fortifying acid, equivalent to 72,345 lbs. of 100% nitric acid. The nitrogen in the nitrocellulose produced averaged 12.66%; the estimated weight of pyrocollodion powder obtained was 49,655 lbs., and 49,484 were actually found. The yield therefore of pyrocollodion per pound of dry cotton is 1.35 and of powder per pound of dry cotton 1.46; therefore each pound of powder required 0.684 lb. of dry cotton; 0.722 lb. of cotton as received; 1.46 lbs. of 100% HNO_3; and 3.01 lbs. of fortifying acid.

According to T. Moreul,[3] the cellulose most suitable for the

---

1. E. P. 24336, 1913; abst. C. A. 1915, **9**, 1251.
2. Quart. J. Liverpool Univ. Inst. of Commercial Research in the Tropics, 1907, **2**, 32; abst. J. Soc. Dyers Col. 1907, **23**, 192; J. S. C. I. 1907, **26**, 605.
3. Bull. Sci. Pharmacolog. **20**, 101.

manufacture of the French smokeless powder, is short cotton fibers stripped from the seeds from the crushing plants, the dead and immature fibers having been removed during the crushing process.

It has been claimed that cotton grown in a cold, wet season, where the growth has been slow—as indicated by the thickened cellular wall and smaller inner filamentous canal—does not as readily esterify as a cotton grown in a locality more favorable as regards humidity and high temperature, and these differences are also reflected in the shorter fiber.

In the method as described by I. Kitsee,[1] the cottonseed is first subjected to a treatment whereby the hull is broken and the kernel separated. The hulls and the adherent fibers are then nitrated, the nitrated product treated with a nitrocellulose solvent, and the solution is separated from the hulls and other undissolved portion by filtration. There is a question as to the stability of such a product.

O. Kress and S. Wells[2] are authority for the statement that cottonseed as delivered to the oil mills, contains about 200 lbs. of adherent fiber per ton. From this a first cut of 75 lbs. of linters is taken, having sufficient length for use as a stuffing material. Afterwards, a second cut of linters of 75–100 lbs. per ton may be removed by means of carborundum wheels or plates, and this lint, being almost free from hull particles, is easily purified for paper-making purposes. The seed is then decorticated, and the residual hull fibers are shaved or cut off by treatment in steel attrition mills; this material is very specky. The average length of the linters fiber is 4.62 mm. (max. 25.44; min. 0.80 mm.), and the average length of the hull shavings fiber 2.41 mm. (max. 8.00; min. 0.51 mm.). According to another process, after the removal of the 75 lbs. of lint with the ordinary linting machine, the second cut with carborundum wheels is omitted, and the seeds are directly decorticated, about 75 lbs. of hull fiber being then removed by the steel grinding or attrition plates. This hull fiber resembles the shavings in length of fiber and contamination with shell particles. A number of samples of these various products have been treated for the manufacture of paper pulp. This class

---

[1] U. S. P. 789978, 1905; abst. J. S. C. I. 1905, **24,** 686.

[2] Pulp and Paper Mag. 1919, **17,** 697, 726; abst. J. S. C. I. 1919, **38,** 858-A.

of material is best treated in a rotary type of digester, and it is extremely important to allow sufficient digester space to permit of efficient circulation of the liquor. Not more than 11 lbs. of dry weight of material should be packed per cu. ft. of digester space, and at least 52 galls. of liquor per 100 lbs. of material should be used. For the elimination of specks, high temperatures of digestion are necessary, with pressures of 80–100 lbs. per. sq. in., the time of digestion being 4 hours. The quantity of caustic soda required varies according to the degree of contamination with shell particles. Cotton linters requires about 9% NaOH on the dry weight of the material; the yield is 90% of boiled pulp, but is reduced during washing and bleaching, owing to loss of short fibers, to about 70% of bleached paper calculated on the basis of dry weights. Cotton shavings require about 12% NaOH and yield 70% of boiled pulp, which is reduced to about 55% in the finished paper. Hull fiber requires 18% NaOH and yields 65%–75% of pulp, or 47%–51% of finished paper, which is suitable for nitration purposes.

In a comprehensive article, J. Wallace,[1] has pointed out, how, in the United States, cellulose for nitration is manufactured from a mixture of 75% of cotton linters and 25% of cottonseed hull fibers. The materials are blended in the "devil duster" machines, into which the cotton is fed from the bale-opening machines. From the dusters it is blown over into storage bins each capable of holding a charge of 6500 lbs., sufficient for one digester of 1200 cu. ft. capacity. For this quantity of cotton, 1360 lbs. of caustic soda is employed, equivalent to 21% of the weight of the cotton, the caustic soda solution being mixed with some of the "black liquor" from a previous charge. The total amount of digestion liquor is about 825 cu. ft. and this is heated to the boiling point before passing to the digester. The digester has a perforated false bottom and the circulation of the liquor is effected by a centrifugal pump through an external heater. The liquor is circulated through the cotton and the heater until it reaches 160° C. corresponding to a steam pressure of 72 lbs. per sq. in.; thus no live steam is admitted to the digester and the concentration of the liquor is not reduced. When the temper-

---

1. Paper, 1919, **23**, 34; abst. J. I. E. C. 1919, **11**, 391; C. A. 1919, **13**, 1016; J. S. C. I. 1919, **38**, 569-A.

ature of the charge has reached the desired point, the circulation is stopped and the charge is allowed to stand under pressure for a given time. Afterwards, live steam is admitted to the digester, the pressure is raised to 100–110 lbs., and the whole charge is blown over into a diffuser. The time of heating up is about 1$^1/_2$ hours and the time under pressure about 2 hours. In the diffusers the black liquor is drained off and the cotton is washed by downward displacement, first with weak washings from a previous charge and then with hot water. The washed fiber is discharged from the diffusers into a stuff-chest below, where it is stirred and suspended in water. Thence it is pumped to a washing engine where it is further washed and the excess of water is removed. The thickened charge is then transferred to a bleaching engine holding about 7000 lbs. of dry fiber, and bleached with about 2.5% of bleaching powder at a temperature of 36° C. for about one hour. Finally the pulp is acidified with about 30 lbs. of sulfuric acid and washed in drainers with warm water. The washed fiber is stirred with water in a stuff-chest and pumped over on to a "wet-end" or rinsing machine at a concentration of about 1% of fiber. The water is squeezed out and the fiber, after going through a picking machine, is delivered on an apron, 8 feet wide and 90 feet long, on which it is dried by hot air from steam coils. Each dryer has a capacity of 800 lbs. of cotton per hour with steam at 75 lbs. pressure. The "white water" is used again for diluting the stuff and any excess is discharged through "save-alls." The recovery of soda from the black liquor is performed in the usual way, the use of black liquor in the digester charge facilitating the recovery process by maintaining the strength of the solution.

According to E. deSegundo,[1] in the treatment of cotton seed in the United States, the textile or "staple" fiber is first removed by the process of "ginning," either by pulling the fibers off the seeds by means of rollers between which the seeds cannot pass, or in the case of the "saw gin" by tearing them off by means of a toothed rotary disc. The seed then retains after ginning about 10% to 12% of its weight of residual fiber consisting partly of

---

[1] J. S. C. I. 1918, **37**, 118-T, 172-T; abst. C. A. 1918, **12**, 1601; Ann. Rep. Soc. Chem. Ind. 1918, **3**, 117; J. Roy. Soc. Arts, 1919, 184; abst. J. S. C. I. 1919, **38**, 185-A.

second quality textile cotton but mostly of quite short non-textile fiber.

This seed is next treated by a saw linting machine which produces "linters." The quantity of linters extracted may be varied partly voluntarily, by adjusting the saws closer together or further apart, and partly involuntarily, by the wearing down of the cutting edges. If the latter are sharpened at very frequent intervals, the percentage of linters removed may be maintained at a maximum. So long as linters were employed solely for second grade textile purposes, the commercial yield from the seed was not increased by increasing the quantity of the linters extracted, since the value depended only on the quantity of longer fibers and the short fibers counted only as a diluent of quality. Moreover, in setting the saws to remove large proportions of linters, the saw linting machine is working at an economical disadvantage and further, the shells of the seed are damaged, thereby introducing dirty particles into the product. However, since linters have been largely or entirely used for the manufacture of nitrocellulose, the tendency has been to strip the seeds closer and closer in order to increase the yield of this grade of material and the manufacturer is only restrained by the limits imposed upon him by the necessities of the subsequent oil-extracting purposes. E. de Segundo quotes the following figures showing the quantities of linters stripped from the American seeds in recent years:

Year.....	1898/99	1908/09	1913/14	1916/17
Linters...	24 lbs.	45 lbs.	68 lbs.	148 lbs.

all calculated per American ton (2000 lbs.) of seed.

The effect of the war on the above figures is remarkable, and at one period the U. S. Government made an order that at least 145 lbs. of linters must be extracted per ton in order to maintain the supply for explosives. It is noted, however, that even before the war the tendency was rapidly upwards, owing to the demand for nitrocellulose materials for peaceful purposes.

E. de Segundo contends that the saw linting machine is not mechanically designed for the extraction of such large proportions of linters and that its legitimate function is its original one, namely, to recover the second grade textile fibers which have escaped the action of the gins. He has designed a machine[1] which

---

[1] E. P. 114435, 114450; Ann. Rep. Soc. Chem. Ind. 1918, 3, 117.

detaches the shorter fibers far more effectively in any proportion which may be desired and produces a far more uniform product than the latter-day linters, while avoiding injury to the husks of the seeds.

In the American system of seed crushing for the extraction of the oil, it is not practicable to strip the short fibers entirely. A certain proportion must be left on the seeds for the subsequent operations, but on the other hand, the removal of some of the wool is essential for good crushing, as an excess of seed lint tends to absorb the oil. The de-linted seeds are first decorticated, that is, the shell is split and the kernel liberated. The mixture is shaken on screens and the fibers attached to the shells make them felt together to from a mat which will not pass through the screens. The clean kernels pass through and are pressed, yielding a pale-colored oil and a clean cake, provided the separation of the dark colored shells has been effectively complete. The effect of removing too much fiber in the delinting process is to diminish the matting effect so that some of the husks fall through and contaminate both oil and cake. This defect has been much in evidence in recent years. The separated shells still retain a portion of the short seed-fibers and these are removed by a special treatment depending on friction, the products being cleanly separated into "cotton hull-fibers" on the one hand and perfectly bare shells or "hulls" on the other.

Segundo makes a proposition for a more rational revision of the linter question as it stands at the present day, in order to conserve the maximum values of the products. Taking the seed as it leaves the gins with approximately 11% of the total fiber, he would restore to the saw linting machine its original function and remove only 2% of linters of textile quality. The textile industry can pay higher prices for useful fiber than any of the chemical cellulose industries, and these selected linters, being free from chips of shell, would command a good market. Next, in order to facilitate the crushing process he would remove 3% of "seed lint" by means of his seed defibrating machine, which operating on the whole seeds would yield a cellulose raw material of a purity most nearly approaching that of the raw cotton. Finally 6% of fiber would be left on the seeds for decortication and would be recovered as "hull fiber" after the separation of the kernels. The seed defibrator is capable of stripping the seeds perfectly bare if so desired and it is to be noted that Egyptian and Indian seeds do not carry sufficient short lint to enable them to be crushed by the American decortication process to form a mat. Such seeds have to be crushed whole and the husks are mixed with the cakes. Nevertheless, the Indian seed does contain about 2% of short fiber and the removal of this by the seed defibrator before crushing would yield important additional supplies of "seed-lint" and would be of considerable advantage to the oil industry.

Cotton Hull Fibers. Until about the year 1905, the cotton seed hull refuse, separated on the screens as described above, was practically a waste product of no commercial value, consisting of a matted mass of seed hulls and incidental dirt (86%-88%) and adherent fibers (12%-14%). In some varieties, e. g., Brazilian, and by some methods of delinting, the percentage of fiber ranged as high as 25% of the material, while the minimum which can be expected from improved working may be taken at about 10% of fiber. From this hull refuse, drastic chemical treatments failed to separate even an approximately clean cellulose capable of industrial utilization. The introduction of machines which detached the fiber from the shells by a rubbing action and separated the two components in a uniform condition placed the problem in an entirely different aspect. An account of these products was given in an article by C. Beadle and H. Stevens,[1] from which the following information is extracted.

The machines in question were the invention of P. Minck and E. de Segundo,[2] working at first in collaboration and later independently. One form of the Minck mill consists of a fixed vertical cylinder with a fluted lining, provided in the center with a vertical shaft from which project a number of arms or beaters. The agitation produced by these arms as the material is fed into the top effects a complete separation of the cotton from the husk without reducing the size of the husk particles. The husk being heavy and deprived of its woolly coating, passes to the bottom and is discharged through a grating; the cotton is winnowed upwards into a "cyclone" or other form of condenser, from which

[1] J. S. C. I. 1909, **28**, 1015; abst. C. A. 1910, **4**, 482; Bull. Soc. Chim. 1910, **8**, 523; Rep. Chim. 1910, **10**, 112, 130; Chem. Zentr. 1910, **81**, I, 779; Zts. ang. Chem. 1910, **23**, 852.

[2] E. P. 12718, 1906.

it is discharged to a baling machine. The other ingredients of the seed, if present (i. e., meal, etc.), can be collected at convenient stages by settlement from the air current. A constant supply of cotton seed hulls is kept up by mechanical feed to each mill and the separated ingredients are automatically removed. The various factors of rate of rotation, diameter of the mill, number and forms of beaters and speed, arrived at, after careful study, not only effect the output of the mill, consumption of power and thoroughness of the separation, but also determine the physical character of the fiber produced. Statistics gathered at the time the article was written indicated that from cotton seed hulls yielding at least 10% of the fiber, the American production should amount to about 100,000 tons of this grade of cotton per annum.

Impurities in Cotton. It has previously been stated that raw cotton fiber consists of approximately 90% cellulose and 6% to 7% water, with smaller quantities of oils, waxes, gums,[1] nitrogenous materials, cuticular products, mineral matter and traces of other substances. Weaving mill waste which is in part made up from the sweepings of the cotton mills, is largely used for the preparation of nitrocellulose. This material, unless carefully collected, may contain appreciable amounts of wood-chips, pieces of metal, especially iron, starchy rags, string, colored thread, cardboard, fine stones, seed particles, etc. It may also contain a considerable amount of fly and dust-like cotton.

The substances other than cellulose in the raw cotton, may be removed by the usual chemical methods. In their complete removal there is always the risk, especially if drastic reagents are employed, of slightly attacking the cellulose and forming oxycellulose. Ordinary bleached cotton gives from 0.2%-0.6% of furfural on boiling with hydrochloric acid and this may be taken as an indication of the presence of a small amount of oxycellulose in the cellulose. Some types of cotton waste contain an undue proportion of altered cellulose (from over-bleaching) and thus are unsuitable for nitration. If the oil and substances other than normal resistant cellulose are present in large amounts in the cotton, a more drastic purification is necessary to obtain a pure cotton.

---

[1] For the determination of wood gum in incompletely purified cotton, see M. Freiberger, Zts. anal. Chem. 1917, **56**, 299; abst. J. S. C. I. 1917, **36**, 923; C. A. 1917, **11**, 3445; Ann. Rep. Soc. Chem. Ind. 1917, **2**, 127.

Thus, in the case of linters, a vigorous treatment is necessary to remove resin and seed-husk. With short fiber from the cotton seed, it is difficult to remove the seed husk completely by mechanical means. Even drastic chemical treatment with the unavoidable production of an appreciable amount of oxycellulose and reducing substances still leaves some husk particles. With increased oxycellulose content, there is more difficulty in obtaining a stable product on nitration. In comparative nitrations, a cotton containing appreciable quantities of oxycellulose, gives a lower nitrogen nitrocellulose, with a higher percentage soluble in ether-alcohol, than that obtained from normal cotton.

The experiments of C. Piest[1] show that a nitrocellulose from cotton which has received drastic purification (either excess bleaching or alkali treatment) tends to produce unstable nitrocelluloses as judged by the Bergmann and Junk stability test. To obviate the risk of obtaining oxycellulose a pure form of cotton, such as cop-bottoms or sliver, might be employed. These, owing to the small amount of matter requiring removal, give a very pure material free from oxycellulose. They are, however, too expensive for general use.

The source and nature of the cotton has an important bearing when the material is needed for spinning and for textile purposes generally. When required for nitrocellulose, these different types of cotton containing the normal cellulose, do not show much variation on nitration as far as yield and stability are concerned, although viscosities of the nitrated product may vary. G. Lunge and J. Bebie[2] found practically no difference (when allowance was made for ash) in the yields of nitrocellulose from the following materials with the same mixed acid (H_2SO_4, 63.84%; HNO_3, 16.96%; H_2O, 19.2%): (a) cotton wool, chemically pure, (b) American cotton (middling fair), (c) American cotton (Florida),

---

[1] Zts. ang. Chem. 1908, **21**, 2497; 1909, **22**, 1215; 1910, **23**, 1009; abst. C. A. 1909, **3**, 485, 2227; 1910, **4**, 2570; J. C. S. 1910, **98**, i, 464; J. S. C. I. 1909, **28**, 746; 1910, **29**, 841; Bull. Soc. Chim. 1909, **6**, 232, 1165; 1910, **8**, 1563; Chem. Zentr. 1909, **80**, I, 474; II, 1090; 1910, **81**, II, 508; Jahr. Chem. 1905–1908, II, 973; 1909, **62**, II, 388; 1910, **63**, II, 423; Meyer Jahr. Chem. 1909, **18**, 309; 1909, **19**, 335; 1910, **20**, 327; Wag. Jahr. 1908, **54**, II, 368; 1909, **55**, I, 431; 1910, **56**, I, 493.

[2] Zts. ang. Chem. 1901, **14**, 541; abst. J. A. C. S. 1901, **23**, 527; J. C. S. 1901, **80**, i, 508; Chem. Centr. 1901, **72**, II, 34; Jahr. Chem. 1901, **54**, 893; Meyer Jahr. Chem. 1901, **11**, 316; Wag. Jahr. 1901, **47**, I, 495. In this connection see Lunge and Weintraub, Zts. ang. Chem. 1899, **12**, 441; abst. Chem. Centr. 1899, **70**, I, 1272.

(d) Egyptian cotton, white (Abassi), (e) Egyptian cotton, natural yellow quality. The resulting nitrocelluloses contained approximately 11.6% N, and then were all soluble in ether-alcohol. C. Hake and M. Bell, however, find that the physical condition of the cotton greatly affects the course of the nitration.[1]

During the nitration and subsequent purification of nitrocellulose the majority of the impurities will be removed. The influence of those which remain on the stability of the nitric ester does not appear to have been specially investigated. The fly and fine sand, etc., in the cotton waste will be eliminated during the mechanical purification (see these topics). The larger pieces of foreign material, as wood-chips, etc., are removed by thorough hand-picking before nitration. Some of the foreign matter which passes through the nitration stage may be collected on blankets over which the nitrocellulose is passed during the purification. Metallic iron may be removed from the nitrocellulose by magnets (see Guncotton Purification).

Cop Bottoms. For the manufacture of the lower nitrated celluloses—the collodion cottons used for blasting gelatin, and less often for photographic films and fine pyroxylin lacquers—cop bottoms are often used. This is spun thread in a tangled condition, and is the last portion remaining on the spindle. It is a comparatively long fiber cotton, and makes an excellent nitrocotton. It is usually considered as too expensive for use in nitrocellulose intended for artificial leather, bronzing liquids and smokeless powder.

[1] J. S. C. I. 1909, **28**, 460; abst. C. A. 1909, **3**, 1687; J. C. S. 1909. **96**, i, 457; Bull. Soc. Chim. 1909, **8**, 61; Rep. Chim. 1909, **9**, 398; Chem. Centr, 1909, **80**, II, 903; Jahr. Chem. 1909, **62**, I, 387; Meyer Jahr. Chem. 1909, **19**, 334; Wag. Jahr. 1909, **55**, I, 434; Zts. ang. Chem. 1909, **22**, 1772. For polemic on above see J. S. C. I. 1909, **28**, 823; abst. C. A. 1909, **3**, 2503; Jahr. Chem. 1909, **62**, II, 388. In this connection see C. Hake and J. Lewis, J. S. C. I. 1905, **24**, 374; abst. J. C. S. 1905, **88**, i, 512; Chem. Centr. 1905, **76**, I, 1702; Meyer Jahr. Chem. 1905, **15**, 357.

CHAPTER IV.

PREPARATION OF COTTON FOR ESTERIFICATION.

The various processes and treatments to which cotton cellulose is ordinarily subjected preparatory to esterification—either nitration or acetation—is, in its completeness indicated by the following distinct steps:

1. Raw cotton storage.
2. Bale breaking operation.
3. Pressure boil-off with alkali, followed by washing.
4. Bleaching the cotton, followed by washing and drying.
5. Weighing the cotton batches, and storage until needed for nitration.

A flow sheet of these various steps as exemplifying the preferred practice in the United States is shown in Fig. 2, as carried out at the Government explosives plant at Nitro, West Virginia. The practice in Great Britain is indicated in Fig. 3, showing the method of procedure at H. M. Explosives Plant, Gretna, Scotland.

Weight of Cotton Bales. An American bale weighs from 400–500 lbs. and occupies 32–33 cu. ft. A ton of cotton therefore requires approximately a storage capacity of 4′ × 3′ × 10′. The American bales are said to be badly packed, the covering being made of inferior material often inadequate to protect the fiber. The density of the American bale is approximately 18–22 lbs., per cu. ft., the Egyptian 37 lbs., and the average Indian 45 lbs., while some special Indian and Chinese bales show 55–60 lbs. density.[1] Two and a half times as much Indian bale cotton as American may therefore be stored, given equal storage capacity. There is seemingly no apparent reason why a considerably higher density bale should not be general with American cotton. This improvement may be achieved by replacing the existing steam operated machines by more powerful hydraulic presses. With the Cummins "Medium Rapid" horizontal bale presses,[2] a density of 56 lbs. per cubic foot may be obtained—a 500 lb. bale measuring 9.5 cu. ft. The saving on inland and ocean transportation would be considerable if such high baling were generally employed.[3]

---

[1] "Cotton and Other Vegetable Fibers," E. Goulding and W. Dunstan.

[2] Textile Recorder, Apr. 15, 1918. Textile World Jour. Mar. 16, 1918.

[3] The Engineer, Nov. 23, 1917.

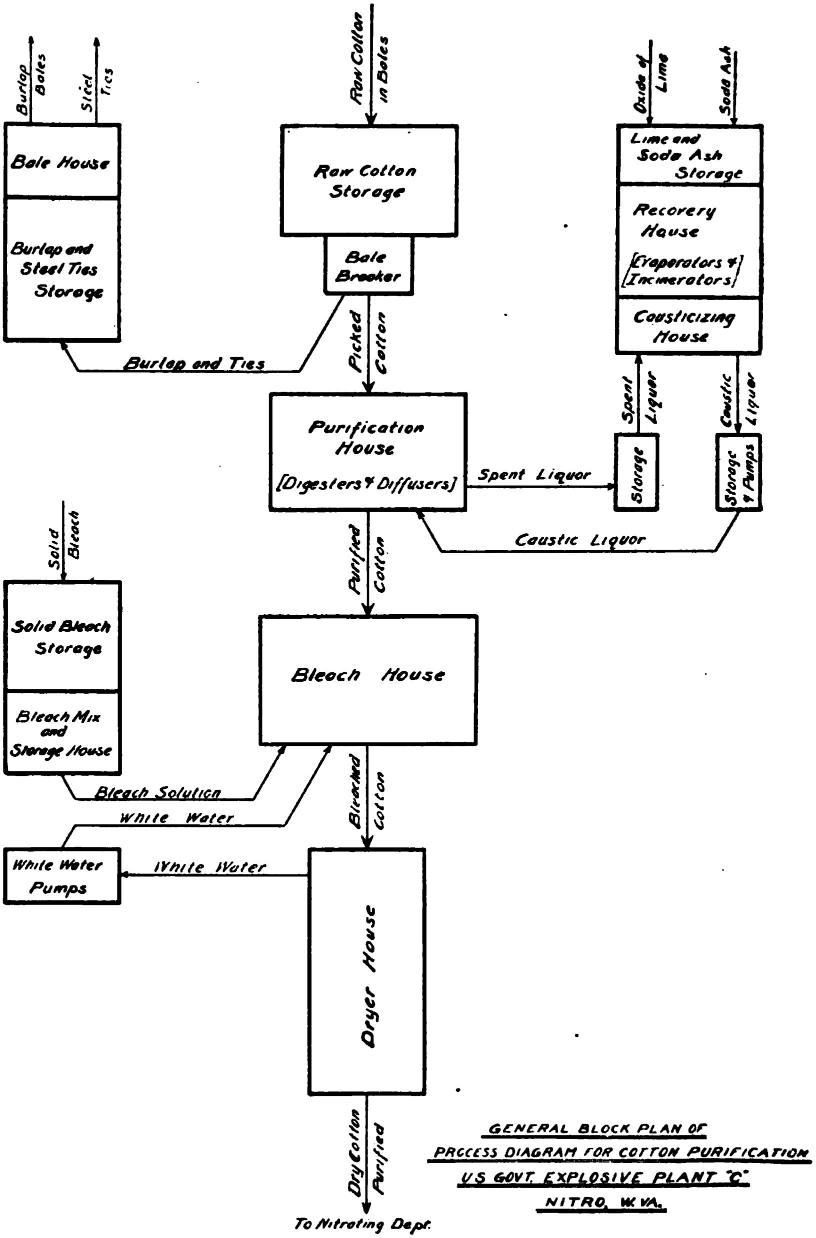


FIG. 2.—COTTON PURIFICATION SCHEME

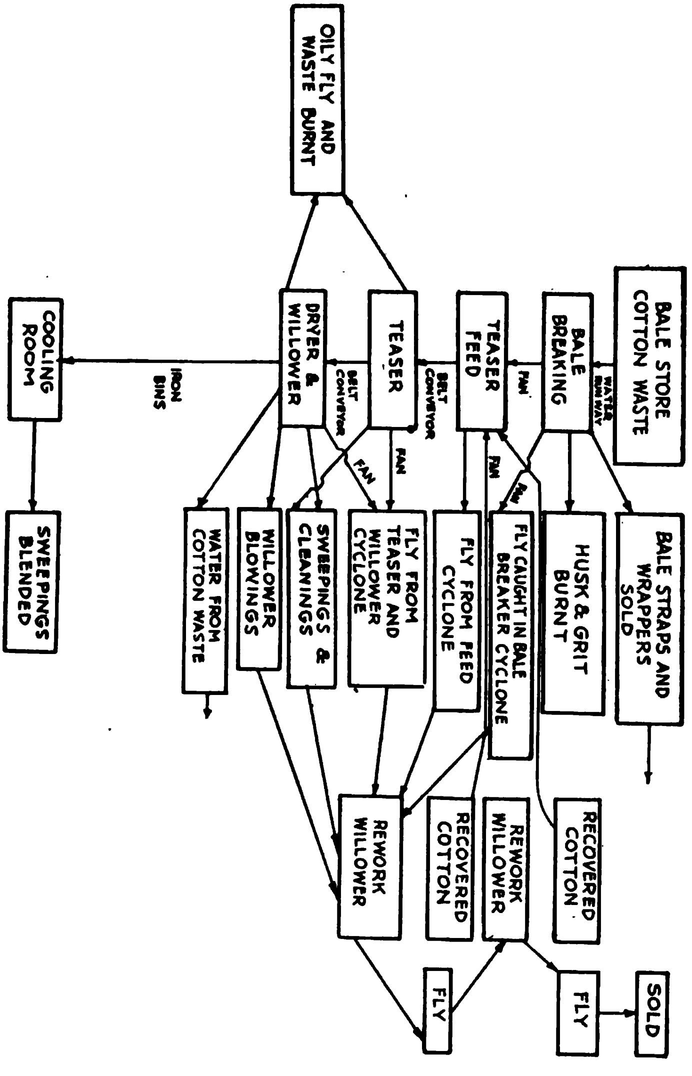


FIG. 3.—COTTON PURIFICATION—ENGLISH SCHEME

The bales of other countries differ considerably from the American standard bale. The Egyptian bale is 700 lbs., the Indian and West African 400 lbs., the Brazilian 200–260 lbs., and the Peruvian 170–200 lbs. The Indian and Egyptian bales are usually well made.[1]

D. Bridge & Co., Manchester, Eng., are manufacturers of the E. Cummins cotton press (Fig. 4) in which the end-way system has been adopted, with one very long filling box, having doors throughout its entire length, and large enough to accommodate the cotton thrown into it. At one end of the box is provided a condensing chamber, at the end of which is attached a powerful hydraulic cylinder working a double-acting ram. By means of multiple rope gearing attached to the ram the required preliminary pressure to pull loose cotton into the chamber is provided on the return stroke. This is accomplished by the use of a follower inside the filling box.

Opening the Bale. Many types of suitable machinery for opening the cotton bale are on the market. The purpose of the machine is to open the bale and mix the cotton waste with other cottons such as card-sliver waste, etc. The waste is drawn directly into the waste hopper and torn up by the action of the spiked apron and combs in the machine. Before being placed on the hopper, spinners' "stick waste" is first run through a thread-extractor and "roving waste" is passed through a machine specially constructed for the economical handling of this substance. The waste hopper may also be used to mix in lower grade or shorter staple bales which may be necessary for distribution among a number of bales.

The hopper breaker, as made by Platt Bros., Oldham, England, is so arranged that it delivers the cotton direct to the lattice of the hopper feeding machine, and dispenses with mixing bins. It substitutes a combing action instead of a roller tearing action and therefore does not damage the fibers. The material is taken from the bale in large pieces and placed in the hopper, the horizontal lattice carrying the cotton forward and pressing it against the spikes of an inclined elevating lattice, where it is subjected to a combing action. It is next carried upwards to a spiked roller which further combs the cotton, and throws back

---

[1] W. Taylor, Textile Recorder, Sep. 15, 1917.

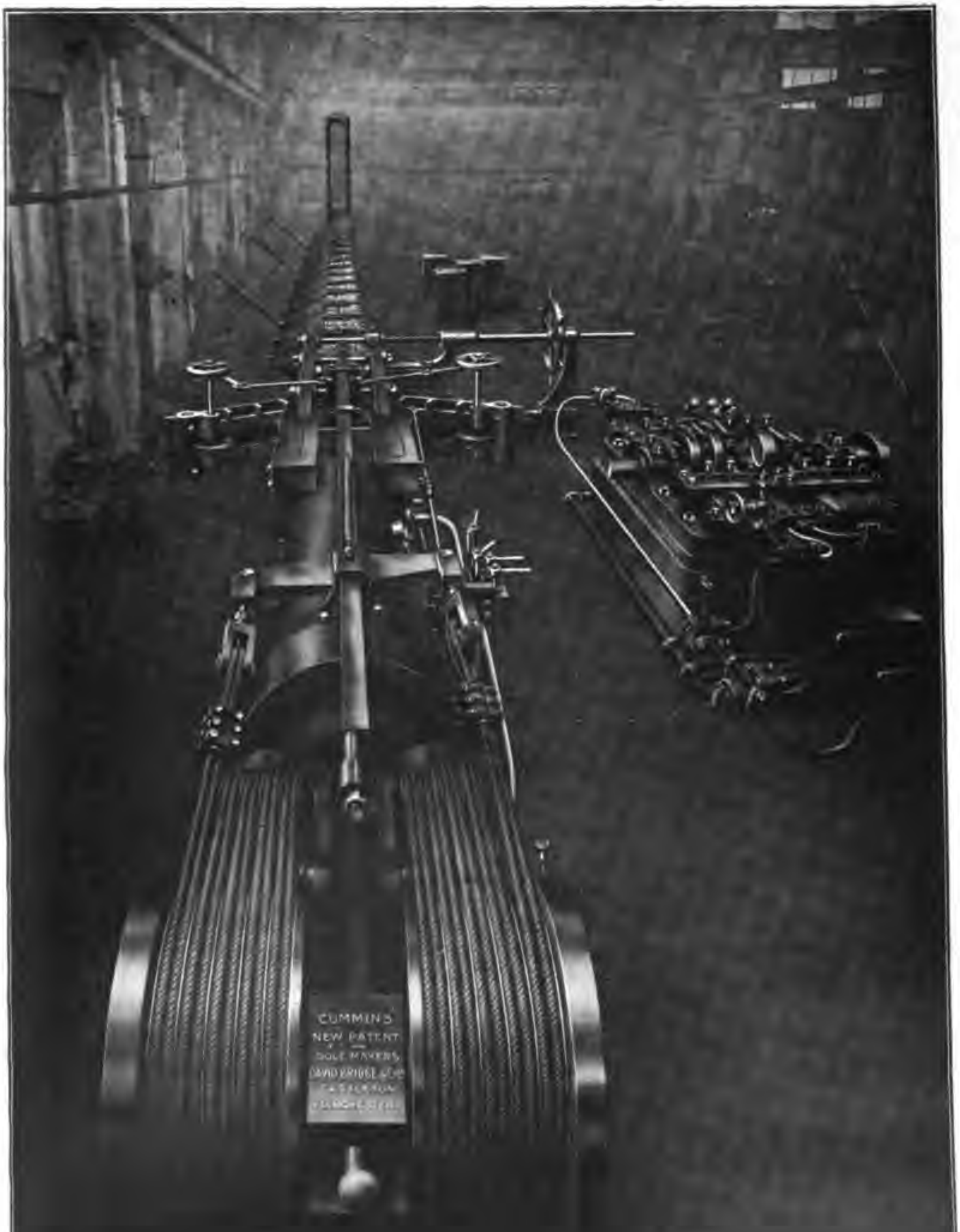


FIG. 4.—CUMMINS HYDRAULIC COTTON BALING PRESS

into the hopper any large or unopened pieces. The spiked roller is stripped and kept clear by a stripping roller, the surplus cotton falling back into the hopper. The cotton, after passing the spiked roller, is stripped from the inclined lattice by a beater and falls on a grid in the delivery sheet. Fans and hoods with reversible grids are supplied to prevent rise of dust and dirt. An improved machine for the blowing room is made by Taylor Lang & Co., of Stalybridge, England. For the opening and cleaning of the cotton they employ a special single-cylinder (Buckley type) opener, without beater (see Fig. 7). The machinery is especially adapted to the treatment of fine material such as Sea Island and Egyptian cotton. Although the machine very efficiently removes dirt, leaf, nep, and other impurities, it does not injure the staple. There is no risk of "stringing" or "nepping," as may occur when the "Exhaust" or "Creighton" type of opener is used. The cotton is combed from the feed roller by blades of the cylinder which are so deposited as to cover the whole length of the feed roller in one revolution of the cylinder. The cotton is thrown by the centrifugal action of the cylinder, revolving at a high speed, against the bars, and the impurities are ejected by a suitable disposition of the bars.

When the cotton waste contains appreciable amounts of dirt, it is advizable to use a machine which combines opening, cleaning, and willowing processes.

In order to obtain a representative sample upon which to perform the usual specification tests, 10% of the bales are usually opened as soon as they are received at the factory. "Grab" portions are taken at different points. After the tests have been concluded and the supplies accepted the cotton is drawn upon according to the demands of the nitration house.

Boil-off. Irrespective of the nature or source, raw cotton always contains an appreciable but variable amount of oily and fatty matter, cholestrin and similar bodies which are insoluble in water and only removable by a saponification, solvent or emulsification treatment. These normally occurring constituents of cotton prevent the latter from rapidly absorbing water, so that such cotton will float on the surface of water for an indefinite period without becoming wetted. That is, *raw* cotton is not absorbent. It becomes necessary, therefore, to remove

FIG. 5.—MECHANICAL HANDLING OF COTTON BALES (GRETNA, SCOTLAND)

these oily and fatty constituents. Several methods have been proposed for accomplishing this purpose, as by solvent extraction, saponification with dilute alkali, or emulsification with dilute acid. In solvent extraction—which is not resorted to ordinarily and only in those instances where either alkaline or acid treatment might be injurious to the cellulose, or the fatty and waxy matter is unduly high—a light petroleum ether, straw colored benzol, or an uninflammable solvent as carbon tetrachloride or acetylene tetrachloride (tetrachlorethane) is usually employed.

If the cotton is treated by "souring" before bleaching, the impurities are emulsified by boiling under pressure with dilute acid—usually hydrochloric, the cellulose being washed with cold water after the treatment until the wash waters are substantially neutral. In the B. Leech method,[1] pectic and other matters are removed by treatment with HCl at or near the boiling temperature, the amount of acid to be used being such as will completely remove all extraneous matters, but insufficient to detrimentally affect the fiber, the amount to be used being predetermined by preliminary tests. A slight alkaline wash is recommended in this process as assisting in the removal of organic impurities and soluble chlorides,[2]

Where the fiber is submitted to an alkaline instead of acid treatment, the operation is known as "scouring," and chemically is a saponification with sodium hydroxide or carbonate, sometimes aided by the addition of smaller amounts of sodium silicate (water glass). All cotton before nitration must be submitted to a process for the removal of fatty and waxy products, i. e., it must be rendered absorbent. In general, unless immense quantities of cotton are esterified at one place, it is most economical and satisfactory for the scouring to be done by those who make a practice of this branch on a large scale.[3] The process of scour-

---

1. U. S. P. 1263685, 1918; abst. C. A. 1918, **12**, 1703; J. S. C. I. 1918, **37**, 332-A; Mon. Sci. 1918, **85**, 77. E. P. 104202, 1916; abst. C. A. 1917, **11**, 1911; J. S. C. I. 1917, **36**, 45; Ann. Rep. Soc. Chem. Ind. 1917, **2**, 165.
2. J. Garcon, Textile World Record, 1914, **48**, 76.
3. On the surface of the individual fiber there is a protecting layer of wax and oily matter, while in the central canal is the dried remains of the protoplasmic material. The object of the boiling out and scouring processes, is, of course, the removal of these materials. When purified from adhering fatty and waxy materials the cotton becomes very absorbent, which quality is explained on the supposition that the ripe cotton fiber is made up of a series of tissues of cellulose, separated by intercellular material, in this way forming a series of capillary surfaces capable of inducing considerable capillary attraction upon any liquid in which the fiber may be immersed.

Fig. 6.—Cotton Dry House (E. I. du Pont de Nemours Co.)

ing—of course—has for its object to render the cellulose more susceptible to reaction with nitrating agents, and to produce a more uniform and stable cellulose ester.

The scouring operation is best carried out by heating cotton in any physical form, under pressure with dilute sodium hydroxide or carbonate solution, either one or both, for several hours in iron, or better zinc-lined kiers with clamped down covers, at a pressure of from three to five atmospheres pressure for from 5 to 10 hours. After the kier has been loaded with cotton, weights are placed on the top to guard against undue expansion, and in the best practice, the kier is never filled more than four-fifths full for the same reason. Sodium hydroxide has an excellent saponifying power, and sodium carbonate desirable detergent and emulsifying properties.[1]

In the process as elaborated by R. Muller,[2] the material is first treated with an aqueous solution of combined alkaline hydroxide and carbonate. In following out the patented description of R. Roberts[3] the cellulose is "de-gummed" by subjecting to a boiling solution of caustic potash, borax and sal soda, and containing in addition a small amount of saponifiable oil. H. Landell[4] advocates circulating boiling NaOH through the closely packed cotton, the material afterwards being washed and given a dilute acid treatment. The washed material is subsequently agitated and shredded in the upper portion of a body of water so as to allow the foreign impurities to settle out in the quiescent portion of the water, the sediment being drawn off from time to time from the bottom.

J. Daniel and F. Benoist[5] obtain the best results by digesting the raw cotton under a pressure of 1–4 atmospheres with a liquid containing 2% of sodium hydroxide, 1% sodium carbonate,

---

[1] The author's experience is that sodium hydroxide (caustic soda) should never be used, on account of its energetic action on cellulose. (See Viscose.) Crystallized sodium carbonate (10 H_2O) is often employed on account of its supposedly milder action. See J. Parcon, Textile Mfr. **31**, 387.

[2] E. P. 9369, 1910; abst. C. A. 1911, **5**, 3136; J. S. C. I. 1911, **30**, 82. D. R. P. 240037, 1911; abst. Zts. ang. Chem. 1911, **24**, 2335; J. Soc. Dyers Col. 1912, **28**, 75; C. A. 1912, **6**, 2177; Chem. Zentr. 1911, **82**, II, 1563; Chem. Ztg. Rep. 1911, **35**, 576; Wag. Jahr. 1911, **57**, II, 443; Chem. Zts. 1912, **11**, No. 2667.

[3] Can. P. 121639, 1909.

[4] U. S. P. 1222422, 1917; abst. J. S. C. I. 1917, **36**, 544.

[5] F. P. 465571, 1913; abst. J. S. C. I. 1914, **33**, 588; C. A. 1914, **8**, 3502.

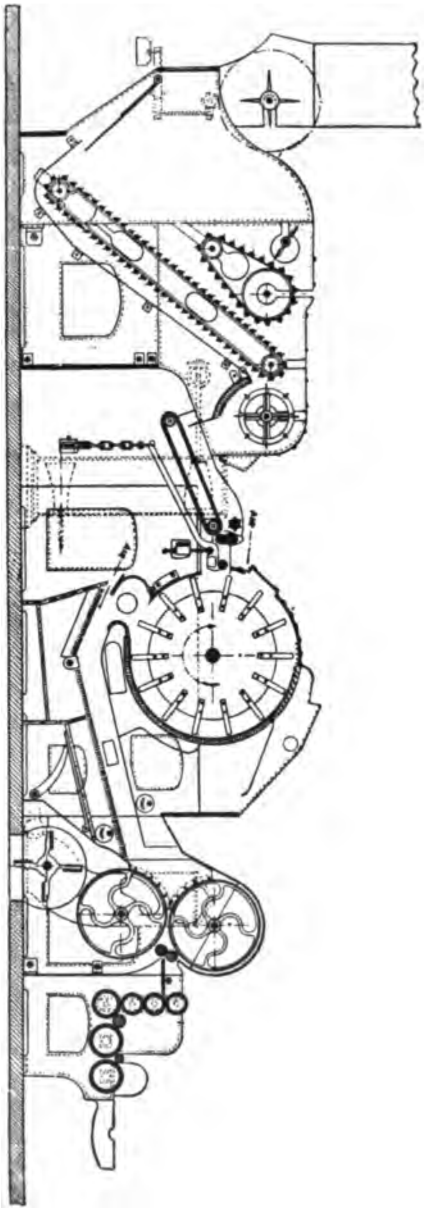


Fig. 7.—Sectional View of Cotton Picking Machine

1% sodium sulfite and 0.1% ethylene trichloride, for 4–12 hours. In the C. Waite patent,[1] the cellulose is digested with caustic soda which has been treated with a small quantity of sulfur so that the amount of sodium sulfide present is less than 0.5%. This small amount of sulfide is said to be sufficient to neutralize the possible effect of the free oxygen present in the formation of oxycellulose, but insufficient to exert an appreciable digesting action.

J. Fair prefers to first treat with a small amount of nascent chlorine generated by the action of HCl on a chlorate, and subsequently boiling in dilute alkaline solution.[2] The fat is removed in the W. Zimmermann process[3] by treating the fiber in a stirring vessel with a mixture of fullers earth, a potash soap, soda, salt and a small amount of ammonia.

In the process of W. Roehrig and designed especially for cleaning cotton for nitration,[4] an emulsion of excess of free fatty acid (or a mixture of fatty acids) with soap is employed as an addition to the de-fatting lye. The treatment of the cotton with lye should commence with a low temperature, preferably below 70°, the mixture consisting of 18.5 k. resin added to a solution of 4.5 k. NaOH in 80 l. of water, the mixture being finally heated to nearly the boiling temperature of water. About 48 l. of technical oleic acid are then added in small amounts at a time, together with about 2.5 k. tallow. After thorough admixture of the several constituents, the emulsion is added to the de-fatting lye. From 2%–4% of the emulsion is sufficient as an addition to a lye which contains 3%–6% NaOH of 12.5° Bé., calculated on the weight of the cotton.

According to J. Foltzer,[5] cotton is preferably boiled under pressure with a solution of sodium carbonate and sodium hydroxide. The product, which, to be properly acted upon by the mixture, should contain at least 12%–15% of moisture. After

---

[1] C. Waite and J. Hedin, U. S. P. 1212158, 1917; abst. J. S. C. I. 1917, **36**, 288; Mon. Sci. 1918, **85**, 4.

[2] U. S. P. 1053125, 1913; abst. C. A. 1913, **7**, 1287; Mon. Sci. 1913, **79**, 151.

[3] F. P. 466806, 1913; abst. C. A. 1915, **9**, 1376; Chem. Ztg. Rep. 1914, **38**, 582; Mon. Sci. 1916, **83**, 71.

[4] D. R. P. 289155, 1914; abst. C. A. 1914, **8**, 2526; Chem. Zentr. 1916, **87**, I, 240; Chem. Ztg. Rep. 1916, **40**, 23, Wag. Jahr. 1916, **62**, I, 255.

[5] F. P. 345687, 1904; abst. J. S. C. I. 1905, **24**, 85; Zts. ang. Chem. 1905, **18**, 434. Mon. Sci. 1916, **65**, 36.

FIG. 8.—COTTON PICKER ROOM (H. M. EXPLOSIVES FACTORY, GRETNA, SCOTLAND)

12–24 hours' treatment, the fiber may, according to the patentee, be washed free from all fatty and incrusting substances.

Notwithstanding the various modifications and alleged refinements as described above, the general arrangement and method of rendering cotton absorbent as a preliminary to esterification, is generally carried on in accordance with the following general or type method: After packing the cotton in the kier, which usually consists of a circular or egg-shaped, upright iron vessel containing a perforated false bottom, and built strong enough to withstand 10 atmospheres pressure, steam is turned on, and the contents of the kier heated to 90°–95°. Where the kier is of cylindrical shape, the capacity ranges from one to three tons of cotton at a charge. An iron pipe is affixed to the false bottom, and rises about three-quarters up the interior of the kier.

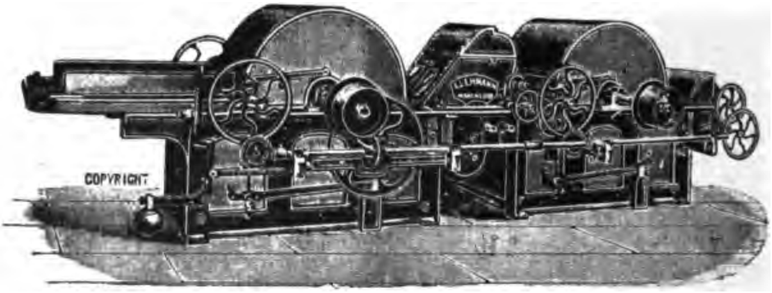


FIG. 9.—THE E. LEHMANN HARD WASTE OPENER FOR COTTON AND ALL VEGETABLE FIBERS

A cowl is placed on the top of the pipe so as to deflect the water in a downward and outward direction, liquid being introduced by an injection apparatus and a centrifugal pump. The liquid is caused to continuously or intermittently (vomiting kiers) circulate through the cotton, usually by means of a steam injector. High pressure steam, for convenience, is used in the heating.

A commonly employed type of kier is shown in Fig. 10, the boiling in this kier being done through hollow trunnions, steam being admitted at one side, and liquid at the other. The apparatus is so constructed that it may be loaded while boiling, and arrangement is provided so that water may at any time be admitted through the trunnions. The liquid passes down to the bottom of the kier and then gradually works up through the mass of cellulose, coming out by a pipe (shown at each side in the illustration), for this purpose. The bleaching tank may be placed in front and below the kier so that when the apparatus is tipped over at an angle of about 45°, the cotton may be dumped out into the bleach tank. The length of time of heating, and the concentration of alkali is determined and regulated by control tests. This apparatus, constructed by the Textile Finishing Machinery Co., Providence, R. I., is extensively used in the United States.[1]

FIG. 10.—TIPPING PRESSURE KIER WITH ENTIRE TOP TO OPEN

When the operation is completed as shown by the laboratory

---

[1] In the cotton treatment process of T. Taylor, E. P. 112969, 1917; abst. J. S. C. I. 1918, **37**, 203-A, the following arrangement is described. In the steam ejector employed, additional steam is admitted into the delivery nozzle to heat the induced fluid, giving simultaneous circulation and heating of the bleaching or other liquor. See also E. P. 2869, 1883; 15174, 1893; 5744, 1915.

tests, the contents of the apparatus is cooled, and the cover raised. The stock is next washed for three or four hours with water, the washing being continued until the runnings are colorless, or at most only pale yellow. The resulting dark colored cotton is then ready for the bleaching process. A usual control test is to remove a sample from the kier, wash and dry and determine the extractive in a Soxhlet apparatus with ether. The ether-extract when evaporated to dryness should not exceed 1% of the weight of the sample taken.[1]

It must be remembered that thorough but not too harsh alkaline boiling is the foundation of successful bleaching, and is of paramount importance where nitrated cottons of high stability are subsequently to be prepared from cellulose. Unless the natural oil and wax are substantially completely saponified and removed by the washing process, a uniform esterification is extremely difficult if not well-nigh impossible. Adventitious grease and unsaponified oil are directly antagonistic to the entrance of nitric acid into the cellulose aggregate, and these bodies materially increase the proneness of the batch to "fume off" in the nitrator. Badly boiled or incompletely "bottomed" cotton, in the earlier days of the nitrocellulose art, were undoubtedly sources of much instability in the nitrated ester produced. It should also be remembered that the incomplete removal of nitrogenous compounds contained in the cotton undoubtedly can cause a similar trouble owing to the power which proteids possess in the absorption of chlorine in the bleaching process, giving rise to chloroamines. Tannic acid if not completely removed may cause slight stains when the cotton is placed in the nitrator, but this is drawing the point rather fine. The pectins, which dissolve in the alkali and are washed out, are intimately associated with the coloring matters of the cotton.

In a series of experiments made by S. Trotman and S. Pentecost[2] it was clearly shown that in a given length of time, less than that necessary for complete action by soda, potassium

---

[1] According to A. Hertzog (Centr. f. Text. Ind. 1890, **21**, 975) the German military authorities require a cotton which when treated with ether yields not over 0.9% fat; when nitrated does not disintegrate; and containing only traces of chlorine, lime, magnesia, iron and sulfuric and phosphoric acids. See also "Inspection of Cotton Waste for Manufacture of Guncotton," C. E. Munroe, J. A. C. S. 1895, **17**, 783.

[2] J. S. C. I. 1910, **29**, 4; C. A. 1911, **5**, 2725; Jahr. Chem. 1910, 1145.

FIG. 11.—COTTON PURIFICATION BUILDING, GROUND FLOOR (E. I. DU PONT DE NEMOURS CO.)

hydroxide will always remove about 20% more than soda, when used in equimolecular solutions. They contend the conditions necessary to secure a satisfactory soda boil are: (1) The water used should be soft (softened water is not as good); (2) The cotton should be regularly and closely packed in the kier so that spaces where steam or air can collect will not be formed, and circulation must be good and uniform throughout the mass. It is recommended to saturate the fiber with the solution before packing to ensure uniform wetting; (3) Good circulation. The degree of saponification varies directly with the cube of the rate of circulation. Dilute boiling NaOH readily attacks cellulose in the presence of oxygen. Of the various types of circulatory apparatus available, the centrifugal pump is probably the best. (4) Absence of oxygen and air. (5) The presence of sufficient soda. No old lye should be used without a determination of the percentage of hydroxide and carbonate present. (6) Rapid removal of the caustic soda after boiling, to avoid the possibility of producing oxycellulose or mercerization due to concentration. (7) Absence of direct contact with steam pipes. (8) Purity of reagents used. In the boiling off process, it is advizable to use a combination of alkaline hydroxide and carbonate, with borax as emulsifiers, with sodium silicate on account of its scouring properties.

The physical changes induced in the cotton as the result of the boiling-off process are stated as: (1) Average loss in weight, about 4.5%–5%. (2) Alteration in the count. The alteration gradually increases with the count, a point not of interest in this connection. (3) Loss in length of fiber is less than 5 %. (4) Increase in tensile strength. Any weakening which might result from the removal of waxy matters is probably more than counterbalanced by the thickening and felting of the fibers. (5) Alteration in twist. In addition to the alteration in the natural twist of the cotton fiber, there is an increase of about 15% in the number of the turns per inch in a yarn.

C. Schwalbe[1] has shown that only cellulose which has already

---

[1] Chem. Ztg. 1910, **34**, 551; abst. J. S. C. I. 1910, **29**, 750. In a subsequent investigation of hydro- and oxycelluloses from wood cellulose (see C. Schwalbe and E. Becker, Zts. ang. Chem. 1919, **32**, 265; abst. J. Soc. Dyers Col. 1920, **36**, 27; J. S. C. I. 1919, **38**, 858-A) it has been found that these substances in common with naturally occurring degradtion products of cellu-

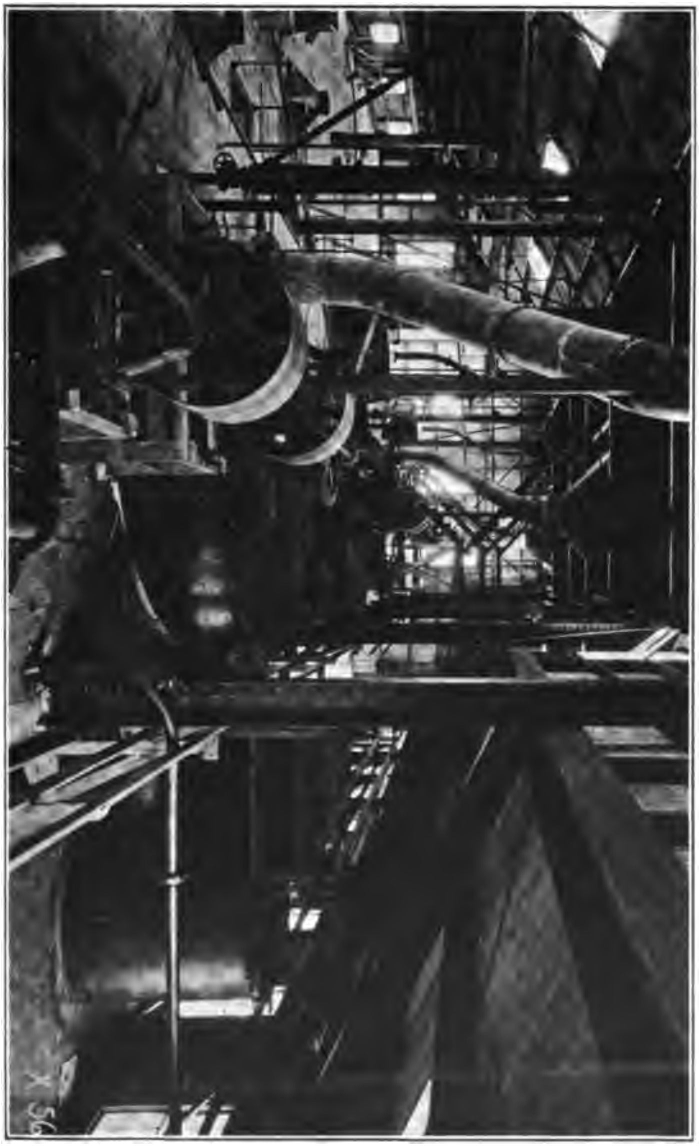


FIG. 12.—COTTON PURIFICATION BUILDING, TOP FLOOR (E. I. DU PONT DE NEMOURS CO.)

been chemically effected by excessive bleaching, etc., undergoes hydrolysis when heated with water at high temperatures. He, together with M. Robinoff,[1] has recorded some curious observations as regards the effect upon cotton when boiled with caustic soda solutions of various strengths and at different temperatures. They tried the effect upon pure cotton cellulose which had been prepared by the method of Tamin,[2] the cotton cellulose having been prepared by boiling pure unbleached Egyptian cotton with alkaline rosin soap solution, washing with hot water and very carefully bleaching. The resulting product had a corrected copper value of only 0.04. It was found that in bleaching the cellulose with hypochlorite solution, followed by "souring" with hydrochloric (or acetic) acid, the formation of oxycellulose was promoted by the use of lower strengths of acids. In addition to determinations of the solubility of the cellulose in dilute lyes, the results of which confirmed those previously obtained (loc. cit.) the "mucilage values" (i. e., the weight of the flocculent matter precipitated by alcohol after neutralization of the alkaline extracts) were also ascertained. Above 150° C., much larger mucilage values were obtained, and hence for this value, too, 150° C. appears to be "critical temperature" in the case of cotton

---

lose, such as cellulose, dextrin, and the hemicelluloses, are converted into mucilage by mechanical means, and particularly by pressure. This mucilage is converted into an irreversible colloid on drying, which has lost the property of swelling in an atmosphere saturated with water vapor. The substances named, by prolonged boiling with water or steaming, are rendered partially water soluble, and lose their property of forming a mucilage. Similar mucilage was prepared by purely mechanical treatment in presence of water and air at 30°–40°. These hydro- and oxycelluloses possess a considerable affinity for mordant bases such as aluminium hydrate. This affinity is so great in the case of the mucilage that the base can be removed entirely from a solution of aluminium sulphate, leaving the free acid in the liquor, by addition of wood cellulose mucilage. Such absorptions are not affected by the base (lime) content of the fibre. Neutral salts such as magnesium chloride are similarly affected. The relation between the moisture content of the atmosphere and the temperature plays an important part in this action, complete saturation of the air with water vapor appears to be unfavorable. In cotton dyeing and in calico printing with basic colors the formation of small quantities of hydro- and oxycellulose is possible and may influence favorably the fixation of mordant and dyestuff. Mucilage formation in mechanical processes during dyeing and printing in the jigger or padding machines seems possible. The sticky lumps formed from the mucilage diminish the permeability. Treatment of the fibre with mucilage for fixing mordants and dyes and for preparing waterproof surfaces may be advantageous.

[1] Zts. ang. Chem. 1911, **24**, 256; abst. J. S. C. I. 1911, **30**, 277.

[2] Rev. Mat. Col. 1908, 313.

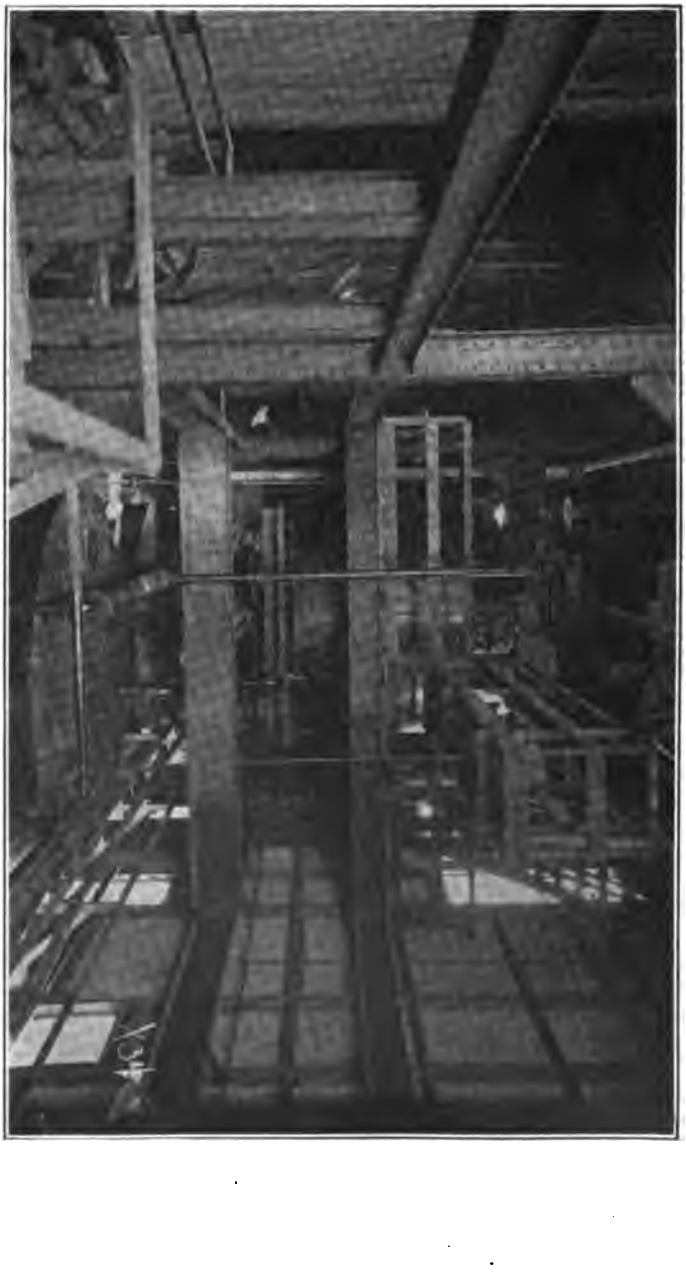


Fig. 13.—Cotton Purification Building (E. I. du Pont de Nemours Co.)

cellulose. A determination of the cotton values of cotton cellulose treated with hot lyes, showed that a concentration of 4% of alkali was (as in the case of cold lyes) the most destructive. The products of hydrolysis formed by the action of 1 and 2 per cent. sodium hydroxide solution appeared to undergo decomposition above 100° C., since there was a decrease in the copper values. In the case of products formed by lyes of 3% strength (or over), this decrease (decomposition) did not begin below 135° C. The decrease in the hydrolysis effected by lyes of 5% strength and over is probably due to the beginning of mercerization (hydration). There appears to be a difference in these respects between different kinds of cotton, American cotton, for instance, giving much higher copper values than Egyptian cotton.

Bleaching the Cotton. After the alkali from the boil-off treatment has been substantially eliminated by thorough washing, the coloring matter remaining in the fiber may be removed by bleaching. Unless the bleaching process be very carefully conducted so as to avoid the possible formation of oxycellulose, it is better to nitrate the cellulose directly after it has been made absorbent, and without any attempt to remove the coloring matter. With linters and other short fibers it is quite customary to forego the bleaching treatment, and to nitrate directly the boiled-off fiber after opening up and drying. With smokeless powder, absence of color in the cellulose is not of great moment, while on the other hand, where the cellulose is to be nitrated or acetated and dissolved for lacquers and the protection of woody, metallic or fabric surfaces, especially those lacquers which are used to protect silver and nickel plated surfaces, it is essential that a thorough bleaching of the cellulose be performed before esterification. These so-called "water-white" lacquers are often made by the nitration or acetation of paper. Where a fairly clear and colorless pyroxylin lacquer is demanded, a partial bleaching only of the fiber is resorted to, the process being known as "half-bleach."[1]

Bleaching is usually accomplished by means of a hypo-

---

[1] C. Piest (Zts. ang. Chem. 1908, **21**, 2497), found that bleaching appears to have a greater effect on the formation of reducing substances than does treatment with alkali, as determined by the reducing action of Fehling's solution on cotton (Schwalbe, C. A. 1907, **1**, 1696, 2179), the oxycelluloses giving lower nitration products than cellulose under similar conditions.

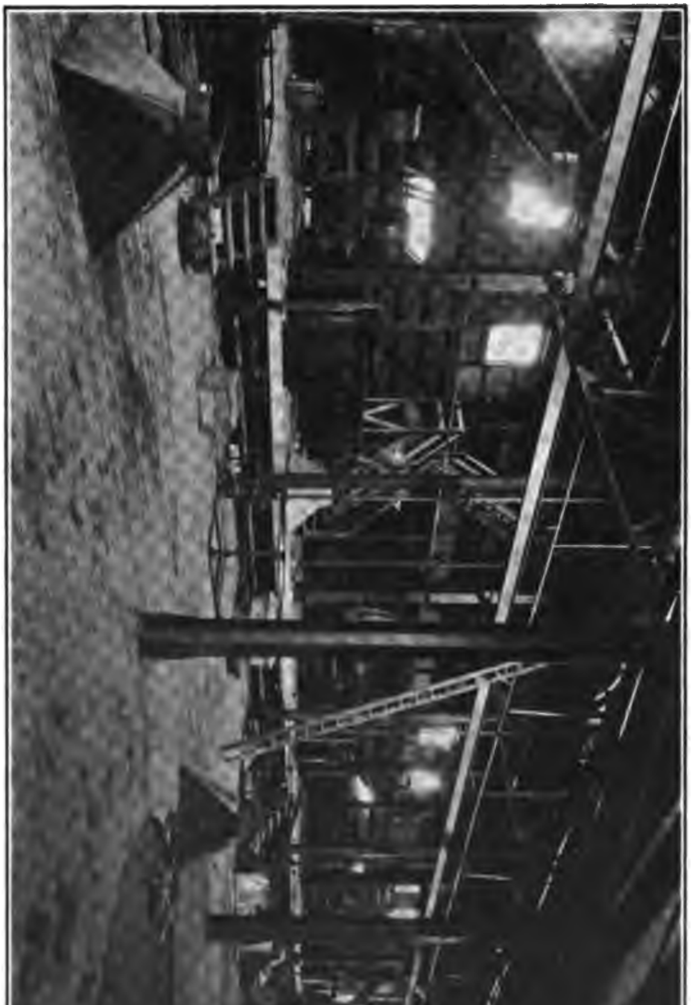


Fig. 14.—Cotton Purification Building, Top Floor (E. I. du Pont de Nemours Co.)

chlorite solution, that of sodium, or more often calcium (chloride of lime?) being used. Where calcium hypochlorite is employed, a stock solution is prepared in which the ordinary commercial bleaching powder, averaging 34% to 35% available chlorine, is dissolved in water and the solution clarified by allowing the insoluble material to subside. From this solution an amount equivalent to about 0.5% available chlorine calculated on the weight of the cellulose is used for bleaching. The fiber is placed in vats or tubs, made either of stoneware slabs, concrete or wooden containers tile-lined, and the bleaching solution pumped over the fiber by means of a centrifugal pump for a period of three to four hours. After this the cotton is washed, still in the same containers, until the wash water gives but a faint test for chlorine with starch iodide paper, when a dilute solution of sulfuric acid or preferably hydrochloric acid is pumped over the material for a period of two to four hours, the cotton being then carefully washed until free from acid.[1]

In the process for treating cellulose as devised by A. de Vains and J. Peterson,[2] a mass is charged through an opening in a cylinder, of preferably reinforced concrete, through which the chlorine is introduced by a separate opening. The mass is then agitated by means of a pump until it is found that the chlorine is well absorbed, whereupon the chlorinated cellulose is transferred to a washing apparatus. This apparatus comprizes a reinforced concrete cylinder having a false bottom of copper or antimony-lead alloy having a siphon and a cock together with a suitable pump and connections. As soon as the cellulose has attained the proper degree of whiteness, it is flushed away to a bleaching engine where it is treated with calcium hypochlorite.

J. Matthews[3] has recently discussed the bleaching of cotton, including permanganates, peroxides, and perborates, giving comparative costs of various methods together with comparative costs of bleaching, and the proportions of the bleaching materials re-

---

[1] Where bleaching powder has been used, it is exceedingly difficult to wash out all traces of chlorine, a minute trace of which may cause the nitrated cotton to turn slightly acid after drying.

[2] E. P. 19099, 1913; abst. J. S. C. I. 1914, **33**, 746. Wirth, E. P. 2519, 1878.

[3] Color Trade J. 1918, **2**, 53; abst. C. A. 1918, **12**, 2251. See A. Bouret and F. Verbiese, E. P. 24768, 1898.

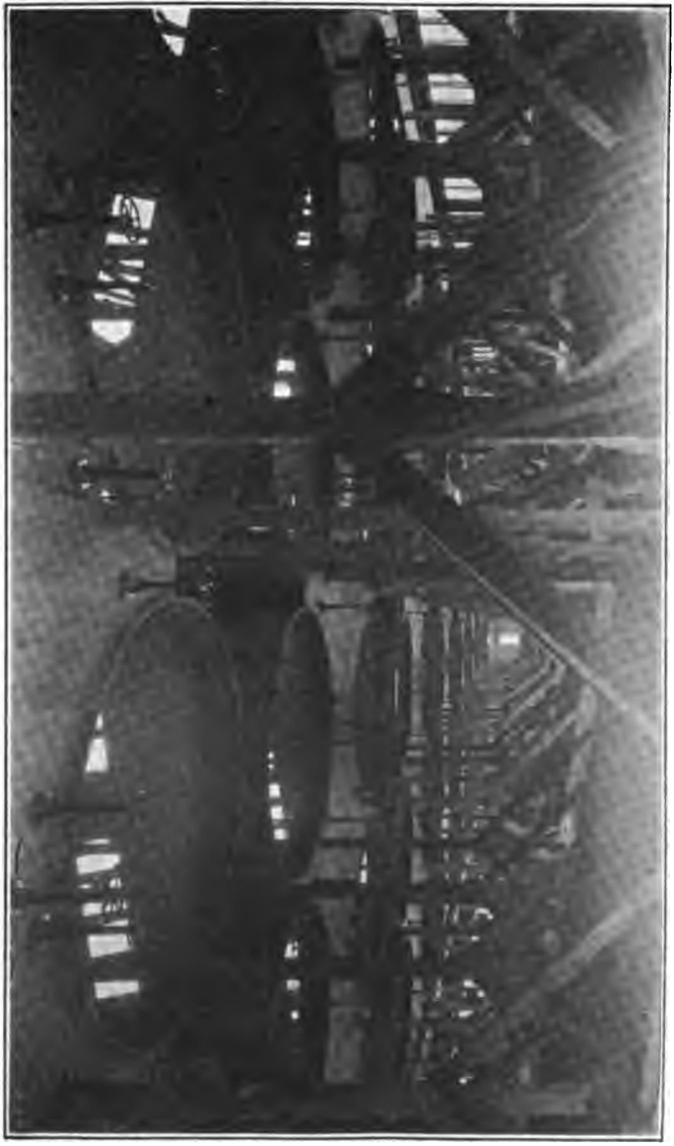


FIG. 15.—INTERIOR FILTRATION PLANT SHOWING TUBS AND VALVE CONTROL (E. I. DU PONT DE NEMOURS CO.)

quired. R. Sansone[1] has emphasized the fact that cotton is best bleached when it is as nearly pure cellulose as possible. This condition according to Sansone, is found after removing the natural fat, wax, and other impurities. The construction and operation of suction and of pressure vats for the rapid bleaching and rinsing are described by him with illustrations and methods of out-door bleaching, and bleaching by ferments. His summary shows that bleaching before spinning is attained with less breaking of the fiber, greater economy in spinning especially for fine, numbered yarns, the production of a pure white cotton and a better control in the purchase of unspun cotton.[2] In the bleaching and purifying process of E. Favier[3] carbon tetrachloride is used as an adjunct to the alkali boil-off and bleaching operation. G. Atkins[4] has described a method for the treatment of cotton with hypochlorite,[5] the claim being made that the silica is also removed by this treatment.[6]

Electrolytic bleaching solutions have also been used in order to hasten the period of bleaching. To hypochlorite and other solutions, A. Lehmann[7] suggests the use of malt or malt preparations, this being added directly to the bleaching bath of hypochlorite. According to him, the successive addition of malt increases the activity of the chlorine so that the bleaching process is rendered twice as rapid and only approximately half the amount of calcium hypochlorite is required. The process requires 2 hours time, after which the material is rinsed, acidified, and the acid removed by washing.

R. Mueller,[8] treats cotton by bleaching with alkali solution with or without the addition of small quantities of metallic com-

[1] Leip. Farber. Ztg. 1914, **63**, 85, 97; abst. C. A. 1915, **9**, 863. W. Mitscherling, Kunst. 1912, **2**, 261, 285, 308; abst. C. A. 1912, **5**, 3185.

[2] S. Higgins, J. S. C. I. 1914, **33**, 902; abst. C. A. 1915, **9**, 246. G. Atkins, E. P. 7058, 1903; abst. Mon. Sci. 1905, (4), **62**, 68; J. S. C. I. 1904, **23**, 385. E. P. 5596, 1901, abst. J. S. C. I. 1901, **20**, 518.

[3] F. P. 368036, 1906.

[4] E. P. 7058, 1903; abst. J. S. C. I. 1904, **23**, 385; Chem. Ztg. 1904, **28**, 732; Mon. Sci. 1905, **63**, 68.

[5] Prepared according to E. P. 5596, 1901; abst. J. S. C. I. 1901, **20**, 518.

[6] Removal of silica by digestion with hydrofluoric acid is never resorted to commercially.

[7] D. R. P. 279993, 1913; abst. C. A. 1915, **9**, 1396; J. S. C. I. 1915, **34**, 657; Chem. Zentr. 1915, **86**, I, 227; Chem. Ztg. Rep. 1914, **38**, 574; Wag. Jahr. 1914, **60**, II, 365.

[8] E. P. 9369, 1910; abst. C. A. 1911, **5**, 3136; J. S. C. I. 1911, **30**, 82, 1727, 1911; abst. J. S. C. I. 1911, **30**, 680; J. Soc. Dyers Col. 1911, **27**, 73.

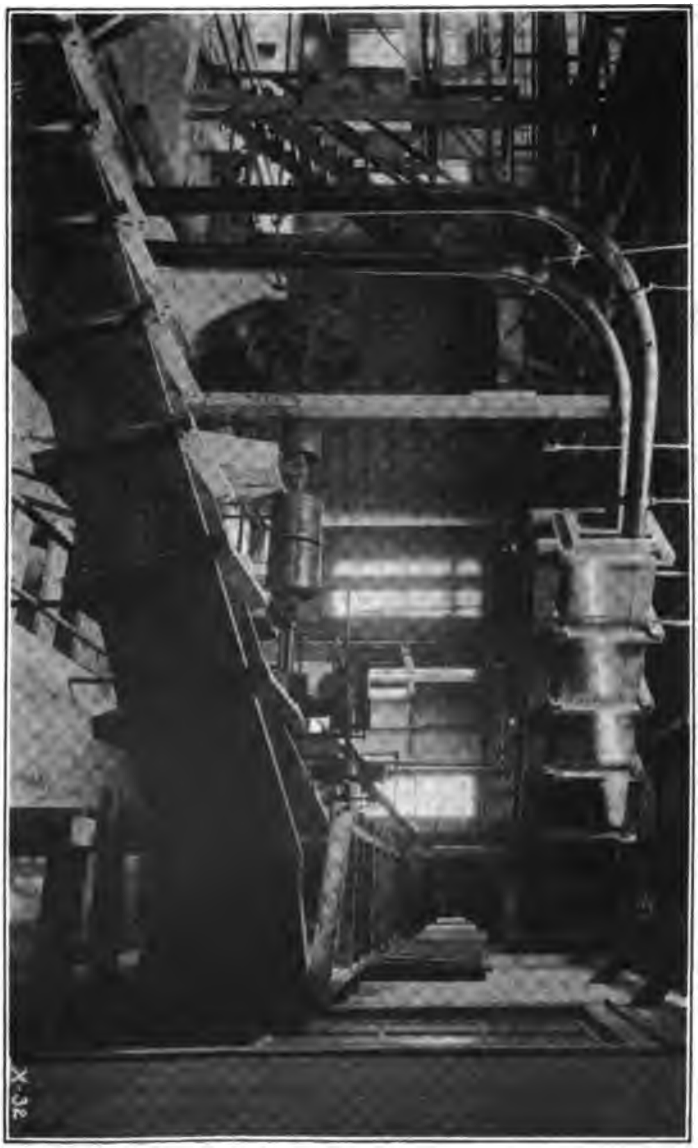


FIG. 16.—COTTON DRY HOUSE (E. I. DU PONT DE NEMOURS CO.)

pounds and with simultaneous exposure to a current of air or oxygen. The introduction of this current being arranged so that direct contact between the gas and the material to be bleached is avoided as far as possible. In an example as cited by him, cotton is boiled for some time under two atmospheres pressure in a solution of sodium carbonate and manganese sulfate in a pressure vat, the material being prevented from floating at the surface, air is then forced into the liquor from above at $3^1/_2$ atmospheres pressure. The darker liquor then becomes lighter and the treating is continued until the liquor becomes practically a light yellow. The bleaching material is then washed, treated with dilute sodium bisulfite solution, washed free from acid and dried. In the method of bleaching as devized by W. Matger,[1]

---

[1] E. P. 8960, 1905; abst. J. Soc. Dyers Col. 1907, **23**, 47; J. S. C. I. 1906, **25**, 864. R. Haller, Zts. Farben-Ind. 1907, **6**, 125; abst. J. S. C. I. 1907, **26**, 523; has studied the structure of cotton as affected by bleaching, mercerization, and dyeing and has found that the fiber, being a seed-hair, has only one end naturally closed, the other being broken off at the point of attachment. The outer wall is covered with a waxy substance, cutin (cuticular cellulose), while dried-up residues of protoplasm coat the wall of the central canal. The peculiar swelling of the cellulose and the bursting and partial breaking away of the cuticle under the action of cuprammonium has been described by Wiesner; the protoplasmic inner wall, like the cuticle, also resists the solvent action of the reagent.

The author has observed that both the cuticle and the protoplasmic layer resist the severe alkaline treatments of the industrial bleaching process, at all events in the great majority of the fibers. The cuticular and protoplasmic layers absorb basic dyestuffs, such as Safranine, and retain the color when washed with boiling alcohol, whereas the cellulose remains unstained. The retention of dyestuff under these conditions is considerable in the case of raw cotton, but decreases in proportion as the fiber is purified; in all cases, however, the cellulose itself remains colorless. The cutin of the cuticular cellulose is completely removed by treatment for half an hour with caustic soda lye of mercerizing strength. When the mercerized fiber is dyed with a substantive dyestuff, the cellulose itself is deeply colored, and on treatment with cuprammonium it swells uniformly and ultimately dissolves, leaving the protoplasmic wall of the central canal as a colored line. The unmercerized fiber, when similarly dyed and treated with cuprammonium, shows a strongly colored cuticle and lumen, and only slightly colored cellulose. It would appear that the cuticle and the protoplasmic wall of the lumen, besides possessing a mordanting property towards basic dyestuffs, constitute layers which also have a strong affinity for substantive dyestuffs, and which, being penetrated by these dyestuffs only with difficulty, hinder the access of the color to the cellulose between them. In this way the author is inclined to explain the darker shades obtained with substantive dyestuffs on mercerized fibers deprived of their cutin. If an unmercerized cotton fiber be treated with cuprammonium, and then washed, and dyed with a substantive dyestuff, those places from which the cuticle has broken away are intensely colored, while those parts which are still protected by the cuticle are only slightly stained. Cuprammonium swells and dissolves the cellulose, leaving the cuticular cellulose unchanged in the form of flakes, whereas strong soda lye dissolves the cutin from the cuticular cellulose, leaving the cellulose portion of the cuticle as part of the normal cellulose of the fiber.

the cotton is treated by confining it in a chamber or cell between sieves or diaphragms, where it is treated successively with boiling alkali, -with water, and with chlorine gas mixed with air, which are caused to successively circulate through the chamber. The bleaching of cellulose obtained from asparagus by treating with alkaline sulfite lyes has also been suggested.[1] In the process of bleaching as elaborated by R. Buggenhoudt[2] the fibers are delivered in a lap or sliver to an endless apron and subjected to successive sprays of a bleaching solution, e. g., sodium hypochlorite. Between the aprons the fibers are conducted through squeezing rollers, the operation of spray and squeezer being repeated until a uniform and complete saturation of the fibers is obtained. These are then automatically delivered from the apron into superposed layers into a tank, where they are steeped until the bleaching operation is complete. Water at ordinary temperature is then run into a tank from the bottom and passed upward through all the layers until thoroughly washed. After the washing is completed, the water is drawn off from the tank and the lap or sliver taken to a hydro-extractor, and is then dried.

The ordinary bleaching process may be carried out in wooden or stoneware vessels.[3] The vessel is fitted, for preference so that the cleansing liquid may circulate through the cotton. The strength of the bleaching solution varies from $^1/_2$–1° Tw.[4] If stronger solutions are employed some oxycellulose may be formed.

---

[1] O. Reinke, D. R. P. 273389, 1912; abst. C. A. 1914, **8,** 2806; Chem. Zentr. 1914, **85,** I, 1796; Chem. Ztg. Rep. 1914, **38,** 301; Wag. Jahr. 1914, **60,** II, 408.

[2] U. S. P. 872097, 1907; abst. Chem. Ztg. Rep. 1908, **32,** 137; J. Soc. Dyers Col. 1908, **24,** 141. In this connection, refer to E. Mann and J. Heess, E. P. 24938, 1913; F. P. 464483, 1913; abst. J. S. C. I. 1914, **33,** 478, 859. F. Dobson, D. R. P. 260306; abst. Kunst. 1913, **3,** 220. Barlow, E. P. 916, 1915; abst. J. S. C. I. 1915, **34,** 10. A. Chaplet, Rev. gen. Chim. Pure et appl. **11,** 314; abst. Chem. Zentr. 1908, **79,** II, 1391.

[3] S. Trotman and E. Thorp, "The Principles of Bleaching and Finishing of Cotton," 193.

[4] To make a solution of bleaching powder, take bleaching powder and stir it up with cold water to a thin uniform paste. Allow to settle a sufficiently long time to have the upper layer a clear yellowish green color. Run this clear liquid off and dilute it with water to a density (by hydrometer) of 1.05. To each 1000 lbs. of cotton rags add 350 gal. bleaching solution and 60 pounds commercial HCl (assuming the HCl is 38% strength). Mix this solution, immerse the neutralized textile in it and let stand all night, next morning take out and wash in cold water until neutral and no chlorine can be detected. If the bleaching powder is not 33% available chlorine and the acidifying acid of strength assumed, errors proportionate to variations in strength of above two will be introduced.

The bleaching solution remains in contact with the cotton for about 1/2–1 hour, the liquid meanwhile being kept in constant circulation. At the end of this period, the solution is drawn off and water circulated through the cotton. In the same container, or more preferably, in another similar vat, the cotton receives a treatment with very dilute acid (1/2 to 1%) preferably with hydrochloric acid. With sulfuric acid there is a tendency to obtain some calcium sulfate in the fiber. The stock is finally washed free from acid, and then passed to the centrifugal wringer for preliminary drying. The bleaching process may also be carried out in a closed rotary vessel,[1] and air, chlorine[2] or other suitable gas added under pressure. To facilitate the entrance of the solution into the fiber, E. Cadvert and A. Jost[3] first evacuate the vessel containing the cotton and then introduce liquor or gas under pressure. By this means the fiber is more readily impregnated. In steaming cotton or flax, C. Cross and Parkes[4] use, in addition to the special hydrolyzing agent, an alkali and a mixture of soap with mineral or other oils. The presence of these latter, it is claimed, effectually aids in the removal of the by-products.

E. Simonsen[5] has investigated the action of bleaching powder on cellulose materials generally. His conclusions were derived from experiments on easy-bleaching Scandinavian sulfite pulp. (a) The action of the bleaching solution is somewhat more rapid in the early stages if the stock is kept agitated, but the ultimate bleach consumption is the same whether the stock is shaken or kept at rest. (b) At fixed concentration the higher the temperature the more rapid is the bleaching, but the bleach consumption also increases. (c) At fixed temperature increased concentration of bleach solution results in increased consumption. The most favorable bleaching conditions are at 20° with a solution containing 0.3% Cl. (d) Nothing is gained in point of time or efficiency by use of excess bleach over that required for re-

---

[1] F. Dobson, E. P. 3801, 1913; abst. J. S. C. I. 1914, **33**, 196; C. A. 1914, **8**, 2482. Addn. to E. P. 3181, 1911; abst. J. S. C. I. 1912, **31**, 225; C. A. 1912, **6**, 1989.

[2] Swiss P. 77516, 1918; abst. C. A. 1918, **12**, 2439.

[3] E. P. 8558, 1894; abst. J. S. C. I. 1895, **14**, 569; J. Soc. Dyers Col. 1894, **10**, 127.

[4] E. P. 25076, 1899; abst. J. Soc. Dyers Col. 1900, **16**, 41; 1901, **17**, 30, 39.

[5] Pap. Ztg. **38**, 3523; abst. C. A. 1914, **8**, 1202.

moval of non-cellulose. (e) Bleached cellulose is very considerably attacked by bleach solutions, especially in the concentrated form. (f) Loss of weight of pulp in bleaching increases with increased temperature, provided total amount of chlorine in the solution is the same; the concentration of the solution has no influence within the limits studied. (g) No advantage is derived from use of acetic acid during bleaching (Lunge's process). The use of acids, especially sulfuric acid, very slightly accelerates the bleaching action but results in increased bleach consumption.

The fact that cellulose is partly altered to oxycellulose was noticed in 1883 by G. Witz,[1-6] E. Berl and Klaye,[7] and E. Berl and W. Smith[8] have also studied the influence of the previous treatment of cellulose, especially bleaching, upon the properties of the resulting nitrates in the laboratory, and C. Piest[9] has subjected cotton to the following treatments: (1) Bleaching for forty-eight hours in bleaching powder solution of 3°–5° Bé.; (2) and (3), bleaching for eight days in solutions prepared by mixing 2–5 k. and 5 k. respectively of bleaching powder with 5 l. of water; (4) mercerization by treatment with 18.5% caustic soda lye for twenty minutes; (5) heating for ten hours at 150° in a current of carbon dioxide.[10] The results obtained showed that with a given nitrating acid and temperature of nitration the nitrocellulose prepared from strongly bleached cotton has a somewhat lower nitrogen content and a considerably higher solubility in ether-alcohol than that prepared from ordinary cotton. The solubility of the nitro-compound in absolute alcohol increases as the cotton is more strongly bleached. Nitrocellulose from strongly bleached cotton is more difficult to stabilize than that from ordinary cotton. The stabilized nitrocellulose is more soluble in

---

[1] Bull. soc. ind. Rouen, 1883, **10**, 416; **11**, 169.

[2] H. Schmidt, Dingl. Poly. 1883, **250**, 271.

[3] Franchimont, Rec. trav. Chim. 1883, 241.

[4] Noelting and Rosenstiehl, Bull. soc. ind. Rouen, 1883, 170, 239.

[5] Nastjukow, Bull. Soc. Mulhouse, 1892, 493.

[6] J. Collie, J. C. S. 1894, **65**, 262.

[7] J. S. C. I. 1907, **26**, 1157.

[8] Zts. Schiess. Spreng. 1909, **4**, 81; abst. J. S. C. I. 1909, **28**, 380; Wag. Jahr. 1909, **55**, I, 431.

[9] Zts. ang. Chem. 1909, **22**, 1215.

[10] D. R. P. 199885, 1908; abst. J. S. C. I. 1908, **27**, 937; Zts. ang. Chem. 1908, **21**, 2233; Chem. Zentr. 1908, **79**, II, 466; Chem. Ztg. Rep. 1908, **32**, 382; Wag. Jahr. 1908, **54**, II, 355; Mon. Sci. 1911, **75**, 93; 1916, **83**, 180.

ether-alcohol than the non-stabilized product. Nitrocellulose from mercerized cotton has a slightly lower nitrogen content, a much higher solubility in ether-alcohol, about the same solubility in absolute alcohol, and is more difficult to stabilize than that from ordinary cotton. Nitrocellulose prepared from cotton which has been heated in a current of carbon dioxide has a slightly higher nitrogen content, about the same solubility in absolute alcohol and in ether-alcohol, and is more difficult to stabilize than than that from ordinary cotton. O. Guttmann,[1] has made experiments during a period of two years with samples of cotton from English and German sources, the history of which is known, from their obtainment from the cotton-spinning works to the finished, and in some cases, stored nitrocellulose. Some of the samples of cotton were unbleached, others had been strongly bleached with bleaching powder, and some were highly contaminated with dust, etc. The results obtained confirm those of Piest, namely, that the stronger the degree of bleaching of the cotton, that is, the higher the content of oxycellulose, the more difficult it is to stabilize the nitrocellulose obtained therefrom, and the more soluble is the nitro-derivative in ether-alcohol, and in addition the solution has a lower viscosity. The view formerly held that in the bleaching process some cellulose is chlorinated[2] is not supported by C. Schwalbe.[3,4]

The ideal bleaching process is one which would completely remove by oxidation or otherwise, the impurities in the cotton, leaving the cellulose completely unchanged. Although cellulose is resistant to chemical action to a great extent, nevertheless during the purification and bleaching process it is slightly attacked. In order not to subsequently produce an unstable nitrocellulose, it is necessary to limit the action of the bleachers on the cellulose within small limits. With the attack of bleaching agents on the cellulose, oxycellulose is formed. The presence of this latter is shown by its properties of absorbing basic dyes more readily than normal cellulose. H. Wrede has worked out a process employing basic dye-products to determine the extent of the

---

[1] Zts. ang. Chem. 1909, **22**, 1717.

[2] C. Cross and E. Bevan, J. S. C. I. 1890, **19**, 450.

[3] Zts. ang. Chem. 1908, **21**, 302; abst. J. C. S. 1908, **94**, i, 138.

[4] Chem. Ztg. 1907, **31**, 940; abst. J. S. C. I. 1907, **26**, 1107. Zts. ang. Chem. 1908, **21**, 302.

bleaching treatment.[1] According to J. Korselt,[2] the risk of formation of oxycellulose in the bleaching process may be reduced by a fractional bleaching of the fiber. Hypochlorite solution is used and the concentration is steadily increased with the progress of the bleaching process. Even when no apparent change is noticeable in cotton which has been bleached without careful control, the material may be altered sufficiently to effect the resulting nitrocellulose.[3] R. Namias[4] has examined samples of cotton which had received excessive bleaching treatment. He found that although the samples showed no weakness of fiber, contained but traces of fatty matter and showed no apparent difference in appearance from good cotton even when examined by the microscope, yet when nitrated for varying periods from 2 to 24 hours, the nitrogen contents of the resulting nitro-products varied considerably. They were incompletely soluble in ether-alcohol in every case because, it is claimed, that they contained unnitrated cotton. Modifications in the compositions of the nitrating bath did not correct this defect. With properly bleached cottons, the results obtained showed that in 2 hours the nitration was complete. The difference between the two types of cotton is attributed to the presence of oxycellulose in the overbleached cotton.

C. Piest[5] employs five methods for the determination of the degree of bleaching of cotton. (a) "Cotton wax method."[6] (b) "*Cu* numbers (Schwalbe's method").[7-10] (c) "Acid number

---

1. Chem. Ztg. 1909, **33**, 970; abst. J. S. C. I. 1909, **28**, 811.
2. D. R. P. 287240, 1913; abst. C. A. 1916, **10**, 2048; J. S. C. I. 1916, **35**, 174; Zts. ang. Chem. 1915, **28**, II, 568; Chem. Zentr. 1915, **86**, II, 768; Chem. Ztg. 1915, **39**, 407; Wag. Jahr. 1915, **61**, II, 270.
3. E. Berl, Zts. Schiess. Spreng. 1909, **4**, 81; abst. J. S. C. I. 1909, **28**, 380; Wag. Jahr. 1909, **55**, I, 431.
4. Mon. Sci. 1918, **85**, 5; abst. C. A. 1918, **12**, 996; J. S. C. I. 1918, **37**, 167-A.
5. Zts. ang. Chem. 1912, **25**, 2518; abst. C. A. 1913, **7**, 895.
6. C. Piest, Zts. ang. Chem. 1909, **22**, 1215; abst. J. S. C. I. 1909, **28**, 746; C. A. 1909, **3**, 2227. See also C. Piest, Zts. ang. Chem. 1908, **21**, 2497; abst. C. A. 1909, **3**, 485.
7. According to C. Schwalbe (Faerber Ztg. 1908, **19**, 33; abst. J. S. C. I. 1908, **27**, 156) overbleached cotton reduces Fehling's solution, whereas with pure cotton cellulose no such action takes place. By estimating the amount of copper produced by the reduction of Fehling's solution, the degree of bleaching of the cotton can be ascertained. A weighed quantity of cotton is boiled with a measured quantity of Fehling's solution, the liquor being well stirred during the reduction. The copper separated is filtered off, washed with hot water, dissolved in nitric acid and estimated by electrolytic deposition; the electrolysis is carried out in a platinum bowl with the aid of a revolving anode. In this way the "copper value" for the sample of

(Vieweg's method.") (d) "Ost's viscosity method" (employing

cotton is obtained. Different varieties of cotton give different figures, those for mercerized cotton being higher than those for ordinary cotton. The "copper value" is referred to dry cotton. The moisture in the sample of cotton is determined by using a toluol drying stove. The estimation is recommended for application in the artificial silk industry.

8. C. Schwalbe, (Zts. ang. Chem. 1917, **30**, 121; abst. J. S. C. I. 1917, **37**, 707; C. A. 1917, **1**, 3430) contends that in order to obtain trustworthy results in the determination of Schwalbe's copper value for cellulose certain precautions are essential. The alkaline tartrate solution should be freshly prepared, since traces of sodium silicate dissolved from the glass will materally increase the copper value. For preparing the solution pure sodium hydroxide made from metallic sodium should be used. It is dissolved in a polished iron vessel which has previously been freed from fat by treatment with alcohol and ether, and the potassium sodium tartrate is added to the cold solution. Old copper sulfate solutions give too high results, and this solution should also be freshly prepared. To avoid solution of silica the distilled water should be kept in a stoneware instead of a glass vessel, and rubber stoppers, which yield particles to the liquid, should not be used. The method of boiling the Fehling's solution in Gnehm's apparatus has an influence on the results. The sides of the flask should be protected against overheating, by means of an asbestos screen, and the liquid should always show numerous steam bubbles. After removal of the burner the supernatant liquid is at once poured into a beaker, and the fibers in the flask are rapidly washed several times by decantation with water at about 80° C., and allowed to stand covered with warm water while the Fehling's solution and washings are being filtered. In this way the further deposition of copper which takes place when dilute Fehling's solution is heated is prevented. Finally the fiber residue is repeatedly washed and removed from the flask. Filtration through paper (No. 595 Schleicher and Schüll) gives more uniform results than filtration through asbestos in a Gooch crucible. The copper is dissolved in nitric acid, and the solution allowed to stand for 1 to 2 days, and filtered shortly before electrolysis. A blank determination should also be made, and the amount of copper obtained should be deducted from the copper value, but only a slight quantity of copper should separate in the blank test.

9. He (Zts. ang. Chem. 1914, **33**, 567; abst. J. S. C. I. 1915, **34**, 23; C. A. 1915, **9**, 23) finds in the determination of the cupric-reducing value of cellulose (J. S. C. I. 1910, **29**, 689), the limits of variation between duplicate tests should not exceed 0.2 in the "copper value," but abnormal results, *e. g.*, values ranging from 0.6 to 1.3, may be obtained through the presence of cupric-reducing impurities in the rochelle salt or the water employed. Commercial specimens of rochelle salt frequently contain small proportions of oxalate, which reduces the Fehling's solution on boiling and discolors the cellulose at the conclusion of the test. Cupric reducing impurities have also been found when condensed steam contaminated with volatile oily matters was used for making up the reagents. The solutions used should always be controlled by a blank test, by adding the hot mixture of 50 cc. of each of the ingredients of Fehling's solution to 400 cc. of water and boiling for 15 mins. under a reflux condenser. The liquid should neither turn greenish in color nor deposit a precipitate of cuprous oxide on standing. If pure normal cotton has been boiled with the mixture, it should show no brownish discoloration. In performing the determinations, the heating arrangements must be adjusted to avoid over-heating of the walls of the flask, as drops of the liquid thrown against the heated glass by the stirrer may be decomposed, forming products which affect the results.

10. Zts. ang. Chem. 1909, **22**, 197; abst. C. A. 1909, **3**, 1143; J. S. C. I. 1909, **28**, 216; Bull. Soc. Chim. 1909, **6**, 552; Rep. Chim. 1909, **9**, 490; Chem. Zentr. 1909, **80**, I, 840; Chem. Ztg. Rep. 1909, **33**, 120; Jahr. Chem. 1909. **62**, II, 385; Wag. Jahr. 1909, **55**, II, 514.

solution of cellulose in ammoniacal copper sulfate), and (e) "The copper sulfate method."

B. Johnsen,[1] in the case of wood-cellulose, measures the degree of bleaching by the action of nitrous acid solution followed by dilute alkali treatment. In the early stages of the bleaching treatment a brown color is produced on a test sample by this treatment; when the bleaching process is complete, however, these reagents give no color with the cellulose material.

The process of bleaching after the cotton is nitrated,[2] has never passed beyond the stage of patent protection.[3]

After the bleaching treatment the cotton is washed with dilute acid (souring) to remove traces of the hypochlorite bleach. This operation is followed by thoroughly washing with water. Some matting of the fiber usually occurs and the cotton may require an opening out (see Teasing).

S. Higgins[4] has observed the rate at which oxygen is evolved from bleaching powder solutions, and from sodium peroxide solutions when in contact with cupric oxide, the oxygen being measured at definite intervals of time. He found that although oxygen was evolved more rapidly from the peroxide solutions, when the results were plotted, the curves were very similar in nature, thus pointing to the similarity of the chemical actions taking place to cause oxygen evolution. The addition of lime to the bleaching solution caused a retardation of O evolution, whereas the addition of small amounts of hydrochloric acid had an opposite effect.

While it is known that the addition of these chemicals to bleaching powder solutions has a similar effect on the bleaching properties of the latter, also the addition of alkali increases the stability of hypochlorites in air, and the addition of acids has a contrary effect. Higgins concludes that during the decomposition in the air, in contact with cupric oxide, or in the bleaching vat, hypochlorites undergo the same decomposition, the oxidizable matter in the bleaching vat merely using up the nascent

---

[1] Papierfabr. 1913, **11**, 979; abst. J. S. C. I. 1913, **22**, 863.

[2] G. Mowbray, U. S. P. 349658, 1886, the pyroxylin being decolorized by a hydrochloric acid acidified solution of oxalic acid.

[3] For structure of cotton fiber as affected by bleaching, see G. Witz, Bull. soc. ind. Rouen, 1883, **10**, 416. Nastjukow, Bull. Mulhouse, 1892, 493. R. Haller, Zts. Farb. Ind. 1907, **6**, 125.

[4] Text. Col. 1919, **41**, 277; abst. C. A. 1919, **13**, 3017.

oxygen which in other cases would ordinarily be evolved.

R. Taylor maintains[1] that with linen, chlorine or hypochlorous acid will not bleach linen, and that a hypochlorite must be present. He alleges that cotton and linen contain two coloring matters of the same general characteristics, a statement brought into question by S. Higgins.[2]

In endeavoring to find a rapid method of bleaching without chlorine or other oxidants, and to avoid the deposition in the cotton fiber which requires careful machine washing, R. Weiss[3] has experimented with the hydroxides of calcium, strontium and barium as saponifying agents, and has been able to show that for molecular equivalents of the three bases, barium hydroxide was less active than the other two, which were about equal to each other. As bleaching agents, the calcium and barium compounds were about equal, but strontium hydroxide was about three times as rapid and more complete than calcium hydroxide. E. Gillieron is of the opinion that the use of strontium hydroxide is impractical on account of cost, and that under certain conditions strontium compounds exercise a destructive action upon the fiber.

E. Cadoret[4] has described an improved process for bleaching depending upon the principle that a liquid or gas injected into the pores of any substance penetrates more completely if it meets no elastic medium in its course, and consequently if the air with which the cotton is impregnated be removed, the bleaching composition will readily take the place of the latter. The A. de Vains process[5] is similar. E. Watremez[6] bleaches cotton fiber by means of a metallic salt whose oxide is soluble in an excess of alkali.

In the patented method of I. Bronn[7] a partial vacuum is employed, the air being withdrawn until the material boils vig-

---

[1] J. Soc. Dyers Col. 1914, **30**, 85; abst. C. A. 1915, **9**, 1120.

[2] J. Soc. Dyers Col. 1914, **30**, 326, 1257; abst. C. A. 1914, **8**, 255, 3369; 1915, **9**, 1120. J. C. S. 1913, **103**, 1816.

[3] Bull. Soc. Mulhouse, 1914, **84**, 499; abst. C. A. 1919, **13**, 76.

[4] E. P. 8558, 1894; abst. J. Soc. Dyers Col. 1894, **10**, 127.

[5] U. S. P. 1106994, 1914; abst. J. S. C. I. 1914, **33**, 916; C. A. 1914, **8**, 3363; Chem. Ztg. Rep. 1915, **39**, 328; Mon. Sci. 1914, **81**, 191. F. P. 449497, 1912; abst. J. S. C. I. 1913, **32**, 482. A. de Vains and J. Peterson, Belg. P. 260042, 1913.

[6] Belg. P. 253529, 1913.

[7] E. P. 12319, 1901; abst. J. S. C. I. 1902, **21**, 857; J. Soc. Dyers Col. 1901, **17**, 210; 1902, **18**, 198.

orously at 40°. In this manner, it is sought to more rapidly exhaust the air from the interior of the cotton filament, and cause a more ready and complete penetration of the bleaching solution without injury to the desirable qualities of the fiber.[1] The opposite effect is produced in the J. Vanlohe method,[2] who first compresses the cotton and then subjects to the action of bleaching liquids. F. Ferrand[3] adds formaldehyde to the bath to protect against the possible formation of hydro- and oxy-cellulose.

In a study of the chemistry of bleaching made by J. Hebden,[4] samples of cloth taken from goods being regularly bleached after the caustic boiling process were examined at different stages with the following results:

PERCENTAGES OF ORIGINAL SUBSTANCES REMOVED AT THE END OF EACH OPERATION

	Steep	First Boil	Second Boil	Chemick	Sour
	%	%	%	%	%
Ash	70.5	87.3	95.4	93.0	95.0
Proteins (N × 6.25)	....	91.5	91.7	92.2	92.7
Fats and waxes (ether extract)	5.5	20.4	64.0	67.8	69.6
Phosphoric acid	60.0	100.0	....	....	....

The samples were also submitted to wetting-out and steaming tests, and it is concluded that the yellowing produced by steaming is due to the proteins rather than to fats and waxes. It is suggested that the bleaching process be controlled by ultimate analyses of the cotton, checked by determinations of ash, and of ether and alcohol extracts.

Preliminary Drying. After kier, bleaching and souring treatments, the cotton may yet receive a "wet-picking." It then

---

[1] Bleachers Assoc. and Higgins, E. P. 131798; abst. J. S. C. I. 1919, **38**, 700-A.

[2] U. S. P. 297319, 1884; abst. J. A. C. S. 1884, **6**, 205.

[3] E. P. 12086, 1914; abst. J. S. C. I. 1915, **34**, 830. The following reports on the bleaching of wood and other forms of celluloses previous to nitration have been issued by the "Poudrerie Nationale D'angouleme," Compt. rend. No. 1, April 6, 1917. No. 39855-6, Sept. 20, 1915. 21521-B6, June 11, 1916; 12156-F6, April 1, 1916; 38008-6, Sept. 8, 1915; 8473-F6, March 5, 1916; 4360-B6, January 30, 1917; 1224-B6, January 10, 1917; 4106-B6, Jan. 29, 1917; 4796, December 27, 1916.

[4] J. Ind. Eng. Chem. 1914, **6**, 714; abst. C. A. 1914, **8**, 3632; J. S. C. I. 1914, **33**, 959.

remains to dry the cotton before nitration. The drying process is usually carried out in two stages. As much water as possible is removed mechanically by rinsing or hydro-extraction. This operation constitutes the preliminary drying. The final drying is carried out by methods depending upon the evaporation of the remaining moisture. (See topic Final Drying.) An efficient type of rinser is made by the C. G. Sargent's Sons, Graniteville, Mass. (see Fig. 17). The machine is fed by an automatic feed into the hopper and from there is gradually and evenly delivered to the rinser. Extending the entire length of the bowl and forming a partition thereby is a perforated brass false bottom, 13 inches from the top of the bowl and below which no cotton passes. Operating above this false bottom and suspended from overhead is the rake or harrow with solid brass teeth which by its action continually passes the cotton, while fully immersed in the washing bath, from the feed end toward the delivery end of the machine. At the forward end of the bowl is an independent rake or carrier which operates at a faster speed than the rake and which further passes the submerged cotton in a thin sheet into the press rolls. The press-rolls are 12 inches in diameter and are made of solid metal. The top roll is wound with some form of resilient material in order to obtain the best results from squeezing. The press-rolls exert a pressure of from 8 to 10 tons and leave the cotton ready for the removal of the residual moisture by the usual evaporation methods. The cotton may receive an intermediate picking between the rinser and the drier.

FIG. 17.—SARGENT DRYING COTTON RINSER

Teasing. As obtained from the factory, cotton waste contains colored threads which must be removed by hand, and often a considerable amount of foreign matter—wood, iron, rubber and

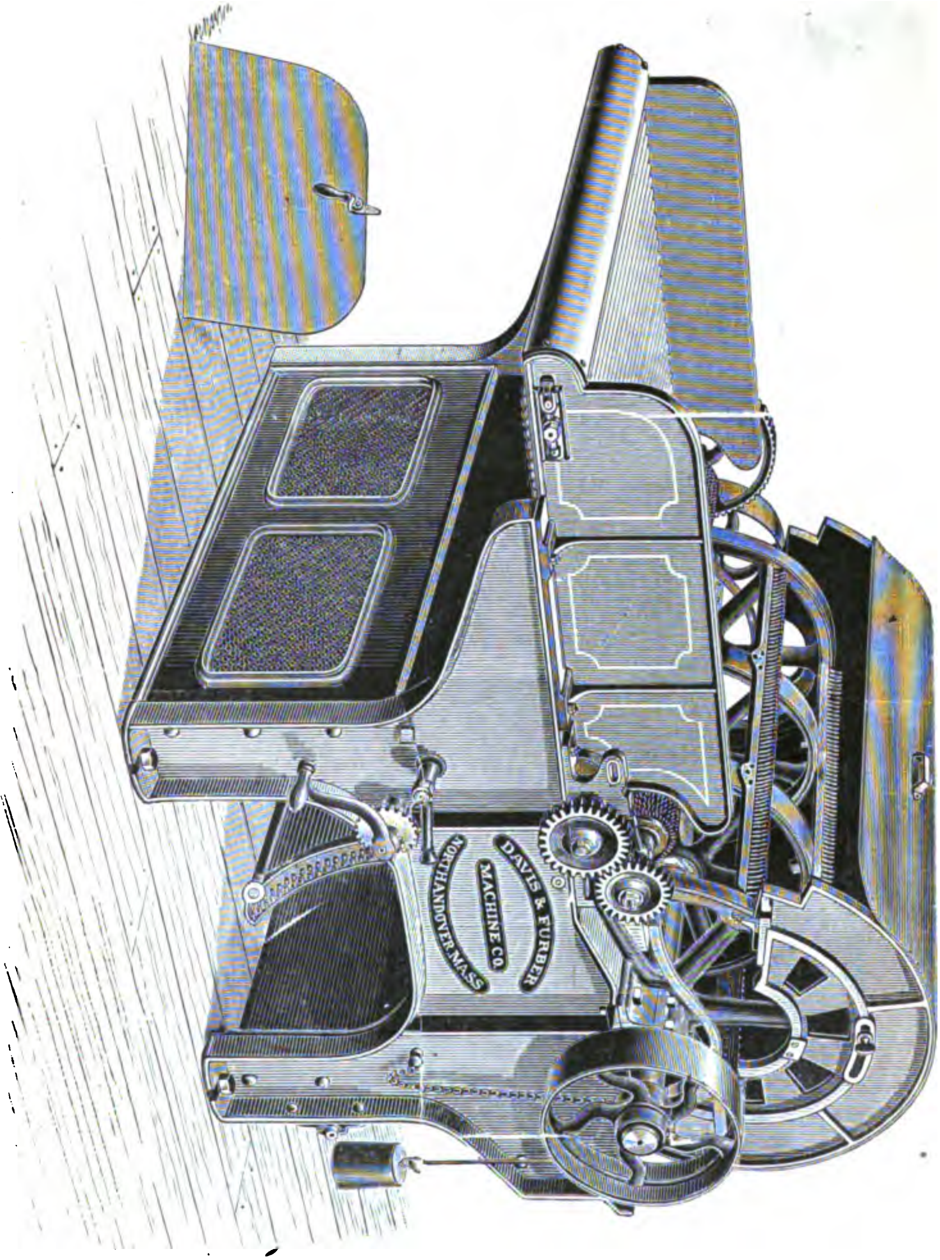


FIG. 18.—THE DAVIS & FURBER MIXING PICKER FOR COTTON

strings—as well as knots and hard lumps. These are removed by a carding machine, where, by means of a series of iron-teeth rollers, the fiber is pulled out and separated, and the lumps opened up. The apparatus of J. France[1] is useful for this purpose.

The form of teasing machine, as used at Waltham Abbey, London,[2] consisted of a combination of rollers armed with iron teeth which separate the fibers of the cotton and opened out knots and lumps. The cotton, as it leaves the teasing machine, is delivered on to an endless band which carries it to the drying machine. The stock, especially if it contains a large amount of foreign material, is again hand-picked in its passage to the drying apparatus. The old procedure, as used in conjunction with the Abel process, was to cut the teased cotton in a type of guillotine into three-inch lengths. This operation is not commonly carried out now, as it was found that the cotton, along the cut edges, was felted together to such an extent as to resist the action of the mixed acids in nitration.

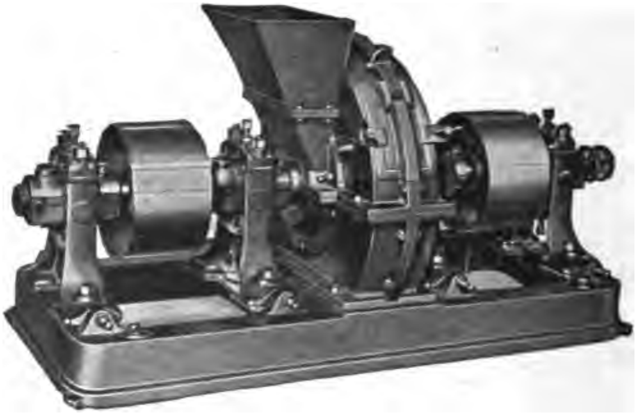


FIG. 19.—COGGSWELL MILL

Where short or long-fiber cotton is used as the source of cellulose rather than cotton waste, two methods of separating and picking are used in the United States, depending on the length of the cotton fiber. For that length corresponding to "linters" and longer, the Davis & Furber "Mixing Picker" with

---

[1] E. P. 20964, 1889; 5364, 1890.

[2] F. Nathan, J. S. C. I. 1909, **28**, 180.

FIG. 20.—SCOTCH PICKER WITH CONDENSER ROLL AND APRON SCREENS DRAWN OUT FROM UNDER CYLINDER FOR CLEANING

pin-feed roll and shell (see Fig. 18) is the type of machine giving most satisfactory results.[1] In recent years, however, the application of cotton has been greatly extended by the gradual use of fibers of shorter length, and for picking such cottons the "Coggswell Mill" (see Fig. 19) has been the type widely used, it consisting of two-ribbed disks revolving at high speed in opposite directions.[2] By means of connection with a Sturtevant or other suction blower and pipe connection to the dry house, which is usually located near the picking house; the cotton, after passing through the picking machine, is automatically carried over to the dry house, where by means of shut-offs located in the carrying pipes in the several drying chambers, the cotton may be blown into any dry-room desired.

The time of beating, during the purification of nitrocellulose, is reduced when the cotton has previously been teased by the methods already given, i. e., material is passed through a Davis & Furber "Mixed Picker," and then automatically by pipes through a Coggswell mill. The Cellulose Manufacturing Co., Waldhof[3] finds that, for the preparation of cellulose hexanitrate, it is advizable to have the cotton not only pure, but as uniformly distributed as possible. After freeing from incrusting matter and all soluble impurities, the cotton is thoroughly dried and

---

[1] The machine is heavily constructed, consisting of a main cylinder fitted with special teeth, together with a feed apron and roll. The cotton is received by the feed apron, carried to the feed roll, the latter holding the stock while the revolving teeth in the cylinder tear it apart. The cylinder revolving at high speed carries the disintegrated cotton around and throws it out at the back of the machine, or into a suction pipe, where it is carried over into the dry house. These machines, which are of large capacity, open up the cotton in such a manner as to make it fluffy and feathery in appearance.

[2] Manufactured by the A. & F. Brown Co., New York City. The mill is run with two belts, one cross and one straight, which drive the grinding disks in opposite directions at a speed of about 2,000 revolutions per minute. All that is needed for the successful operation of the mill is a well built, well balanced counter-shaft for high speed, with a friction-clutch pulley for starting the mill up slowly, and a heavy immovable foundation, so there will be little or no vibration. When properly set up, the mill requires no skilled labor to operate. The only adjustment needed is in the turning of the tail pin one way or the other as the material may be wanted, coarser and finer. After the mill has been running a few months it is good practice to reverse the belts, thus giving a fresh wear to the grinding surfaces. The plates are about the only parts which may require renewing, and under favorable conditions may last upwards of two years.

[3] E. P. 336, 1891; abst. J. S. C. I. 1892, **11**, 180; Mon. Sci. 1892, **40**, 166. In this connection see the disintegration method of treatment of cotton mentioned elsewhere in this work by the Dynamit Akt. Ges., D. R. P. 4410, 1878; abst. Ber. 1879, **12**, R, 712; J. A. C. S. 1878, **1**, 303.

FIG. 21.—SCOTCH PICKER ARRANGED WITH CONDENSER ROLL AND APRON

FIG. 22.—THE W. TATHAM THREAD EXTRACTOR FOR COTTON PICKING

then disintegrated in a specially constructed disintegrator. The stock is passed through the apparatus several times until treatment of a sample of the material with the usual mixed acids gives a product which passes definite specification tests.

Where cotton waste is used composed of card room and spinning room sweepings, roller laps and similar materials, which are composed of "soft" waste mixed with a fair proportion of threads, a "thread extractor" as shown in Fig. 22 is useful. The machine shown in the illustration is made by W. Tatham, Ltd., Rochdale, England, and takes the place of the former slow and tedious process of hand picking. The material to be treated is placed on the tray attached to the cover of the machine, and is then passed through a funnel at the right-hand side and fixed directly over one of three spiked rollers which are caused to revolve at high speed in order to thoroughly loosen the material so that the "soft" may be separated from the thread waste. The thread portion is retained by the spiked rollers around which they are wrapped, and from which they are periodically removed by a special form of knife drawn by an attendant along a groove in each roller.

In the picking or teasing process, it may be desirable to first break the knots and hard lumps of waste before it is fed into a waste opening machine. By so doing, the waste is rendered soft so that it can be much more evenly fed on the feeder bed or plate. The Garnett Preparer or Knot Breaker shown in Fig. 23, is useful for this purpose. Attention is drawn to the advizability of a thorough opening out of the cotton stock as an aid to uniform and ready nitration.

Willowing. The process of separating or blowing out the fly, dust, etc., and disintegrating the cotton is known as willowing. This operation may be carried out after the bale is opened or after the cotton is dried, depending to a large extent on the type of the cotton waste. A usual form of willower consists of a machine fitted with a revolving drum composed of three cast iron rings keyed on to a steel shaft. To these rings are attached wooden lags each fitted with cast iron teeth. The cylinder revolves at about 350 revolutions per minute and strikes the material down from the feed rollers. Below the lower shaft of the cylinder is fitted a grid constructed of flat steel bars set at a suitable

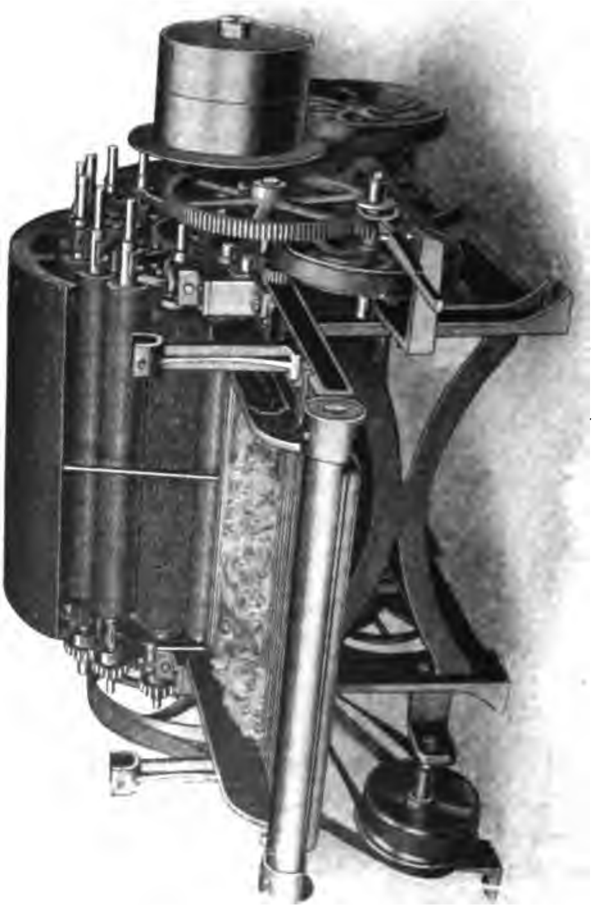


FIG. 23.—THE GARNETT PREPARER OR KNOT-BREAKER

distance apart and through the space thus formed dust and foreign matter fall. Fly and fine material is removed by means of a fan and piping to a large cyclone chamber. The heavier matter which collects beneath the chamber is collected at intervals. Along the cylinder and carried by the sides of the cover are usually two slowly revolving toothed rollers which in conjunction with the cylinder serve to loosen the material previous to delivery.

The willowing machine shown in Fig. 24 is made by J. Hetherington & Sons of Manchester, Eng. It is used mainly with soft wastes (such as lump yarn strippings, roller waste, scutcher droppings, etc.). The machine is fitted with feed and delivery lattices which travel at a uniform speed. The motion of the feed is intermittent, and may be adjusted so as to allow the charge of cotton to remain in the machine for any necessary period, in order to obtain the required cleanliness. The apparatus is fitted with special "willow teeth" by the use of which the cotton is distributed laterally over the periphery of the cylinder, and is disintegrated and cleaned from dirt very effectually. When the bale is opened and the cotton cleaned and willowed, it still may contain cop-cottons and other hard wastes. The material in this condition is not sufficiently uniform for nitration. It is necessary to open these lumps by teasing or picking machinery. The fly and other cotton material which collects in the cyclones is drawn from the machines by the suction of the fan attached to the former. A cyclone is an inverted conical vessel usually about 8 feet in diameter at the widest point and 9 feet in height. The current of air which draws in the fly and fine cotton enters tangentially at the top and gradually falls until at the apex, the fly enters the cupboards from which it may be taken at intervals for retreatment. A chimney to carry away the excess of air passes from the top of the cyclone through the roof.

The fly and other material which gather under the various machines and in the cyclones contain much good cotton and in order to extract this it is retreated in automatic willowing machines. The latter may be similar to the willowers already described, but is fitted, in addition, with a time gearing which operates the feeding lattice at definite intervals and also governs the period of willowing. From this machine three products are obtained. (1) Good long fiber cotton which is blended with current unteased

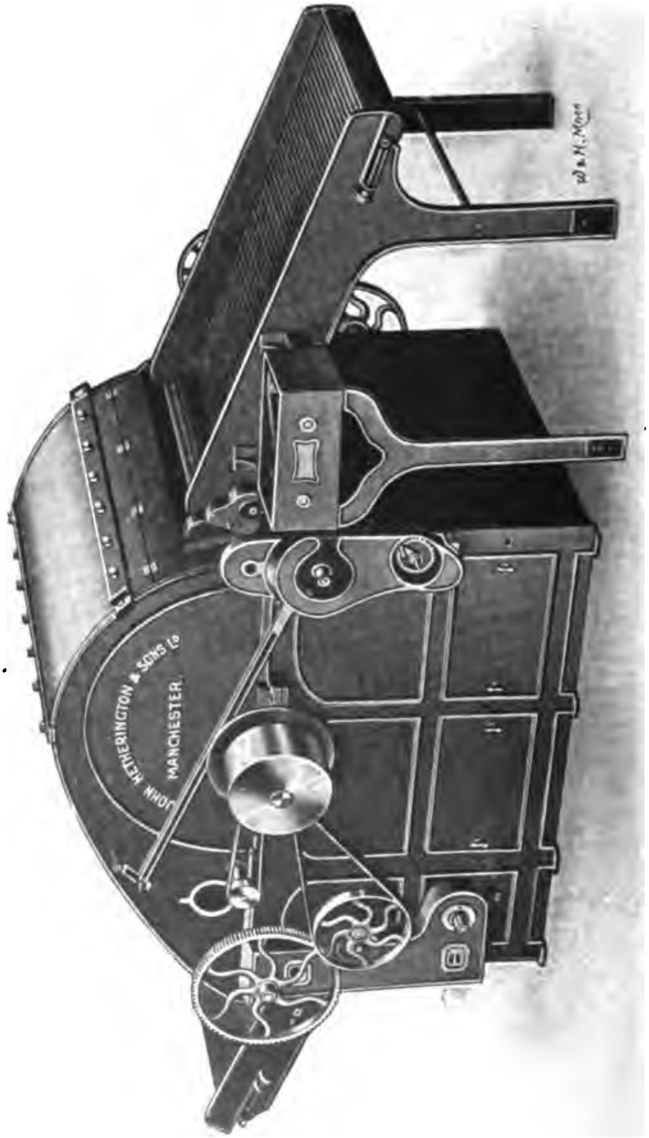


FIG. 24.—HETHERINGTON IMPROVED WILLOWING MACHINE

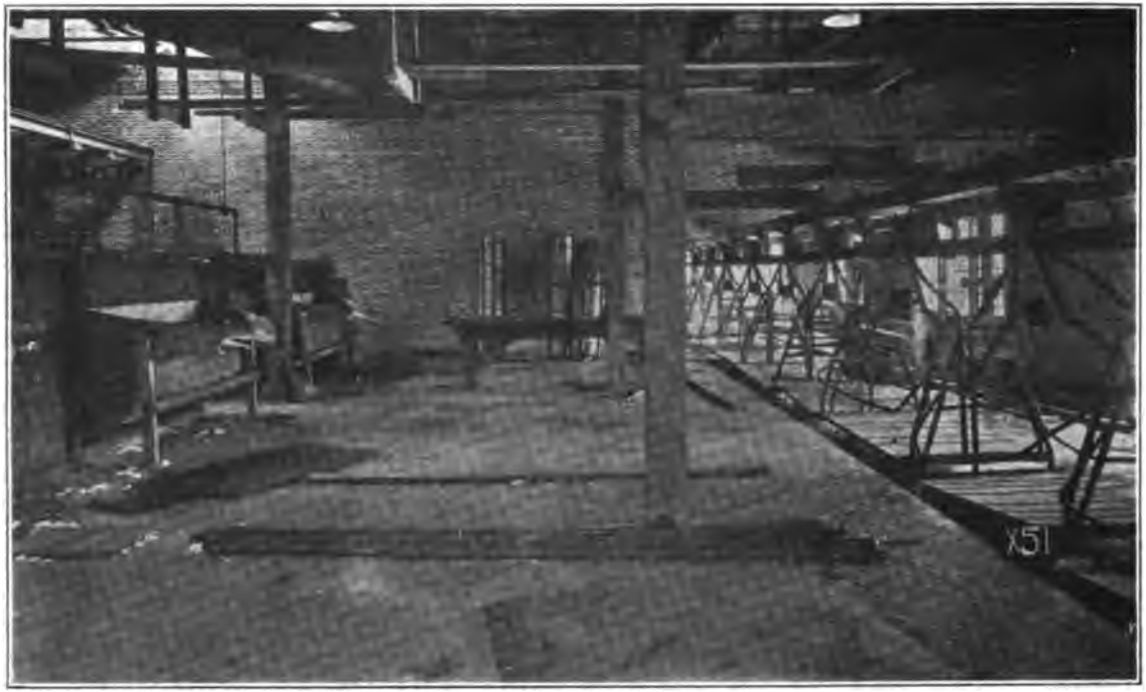


Fig. 25.—Cotton Dry House, Showing Delivery Aprons at End of Dryers (E. I. du Pont de Nemours Co.)

waste. (2) Rejected material containing much grit and sand (Scroll). (3) Fine cotton dust which is abstracted by a fan and deposited in a separate cyclone. The second or scroll portion is again retreated three times in order to save as much good cotton as possible, and an overall recovery, varying from 30% to 50% on the original weight of fly is obtained. In a machine with a 4′ 6″ feeding lattice and a 14″ delivery belt, 0.5 ton of fly may be retreated per day with ease.

Conveying. It is necessary at various periods during the purification treatment to convey the cotton from one machine to another. When these machines are close together, there is not much difficulty in transferring the stock, but in some cases, as when the cotton is sent long distances, there is need for special conveyers in order to save unnecessary handling and labor. Conveyers may be used between each stage in the purification of cotton. They are particularly useful, however, at certain points. After the opening of the cotton bale, the cotton may be sent by a conveyor to the picker. An opener, equipped with such a conveyer, is made by P. Garnett, Cleckheaton. The conveyer at this stage not only saves labor, but prevents the formation of dust in the atmosphere. The cotton is also thoroughly circulated through the fan and in the tubes and exhaust box; in consequence, the blending is much improved.

After the cotton has passed the washers, it requires transferring to the bleachers or steeping boxes. At this stage, conveyers are also useful. Again, after teasing, the cotton will require conveying to the dryers.

An endless band or chain connected together by cross-rods is a type of conveyer often employed. The cotton may also be forced through a pipe by means of a blower from the picker to the dryer.

Another method of conveying is to feed the material into enclosed or open pipes or troughs through which liquid flows carrying with it the cotton material.[1] The pipes or troughs may be mounted on pivots so as to be capable of inclination in either direction and may be provided with outlets or gates for discharge

---

[1] T. Taylor, N. Beswick, E. Jenkins, E. P. 104214, 104524, 1916; abst. C. A. 1917, **11**, 2048; J. S. C. I. 1917, **36**, 451.

FIG. 26.—THE "PROCTOR" DRYER FOR COTTON—SINGLE CONVEYOR TYPE

at any desired point[1] in the conveying apparatus or machine.

Final Drying. As the cotton leaves the teasing or picking machines, it invariably contains 6%–10% moisture, and 85%–90% of this moisture should be removed before the nitration stage. If the cellulose is to be acetated, a higher percentage of moisture is permissable. If the cotton is not dried to this extent, it becomes difficult to obtain uniform nitrations, and the fiber is prone to "fume off" during nitration. Furthermore, there is added dilution with water of the waste nitrating acids, and their perpetual rejuvenation, therefore, becomes increasingly difficult and expensive, necessitating the use of nearly absolute nitric acid and oleum. Another point is, that in the nitration of cellulose containing relatively large amounts of moisture, often an undue amount of cellulose passes into solution or suspension in the nitrating acids, rendering special clarification imperative if the acid is to be continually fortified for use again.

It must be remembered that although a cellulose containing but 3 or 4% of moisture may cause but a small alteration in the composition of the mixed esterifying acid as a whole, yet in the immediate vicinity of the fibers the dilution of the acid may be appreciable. With this lack of uniformity it becomes increasingly difficult to control the nitration process so as to obtain dependable esters from the viewpoint of uniformity and stability. Cotton containing much moisture usually gives decreased yields, and such a pyroxylin, when dissolved in such solvents as acetone and amyl acetate, produce lacquers with a decreased adhesiveness to wooden and metallic surfaces. For this and other reasons, it is of paramount importance that for nitration the cellulose should not contain over 1% moisture when immersed into the esterifying bath, and for acetation, the moisture should not exceed 4%, although cotton can be acetated containing a higher percentage of moisture than can tissue paper, other factors remaining the same. However, the question of moisture in the acetation of cellulose is exceedingly important, due to the action of the catalysts and dehydrating agents employed in the normal esterizing bath.

In one method of cellulose drying, the cotton is placed in

---

[1] In this connection, see E. P. 13626, 1889; 5560, 1891; 11929, 1899; abst. J. S. C. I. 1890, **9**, 856; 1900, **19**, 689.

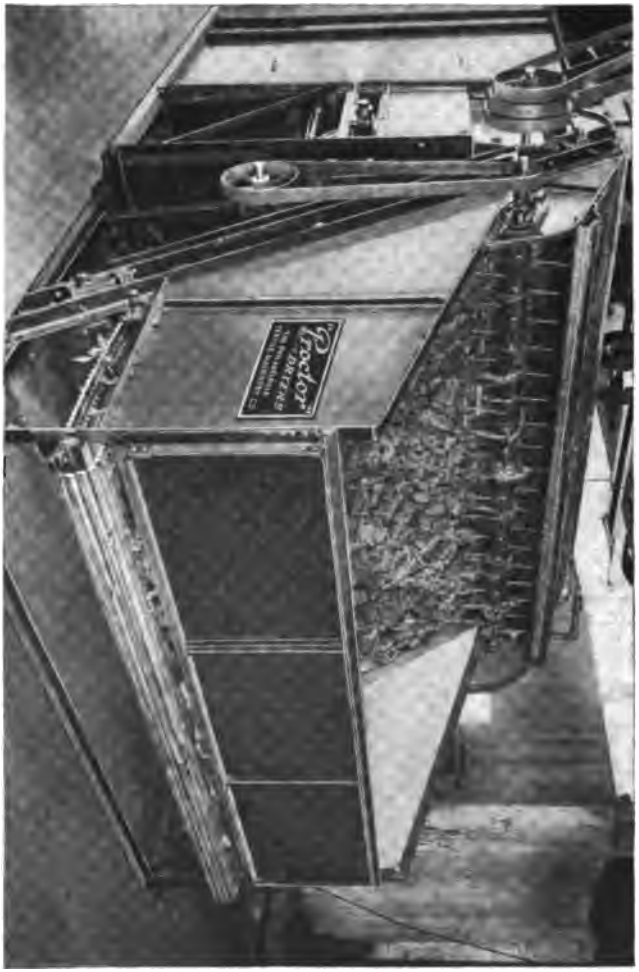


FIG. 27.—"PROCTOR" SINGLE CONVEYOR DRYER SHOWING FEED

large steam jacketed iron cylinders, the circulation of steam in the surrounding jacket being so adjusted that a temperature of 70°–90° is maintained in the interior. It is not customary to dry cellulose for esterification at temperatures above 95°, and preferably between 80° and 90°. This applies particularly to cellulose intended for soluble nitrocellulose (the lower nitrated derivatives). When the latter is to be manufactured, it is inadvizable to use cotton which has been wetted after drying, and then redried. It has been found that the cotton after the second drying is slightly more brittle, especially the outer layers of the individual filament. The difference between a once-dried and a twice-dried cotton can also be detected in the ease and completeness of solution of the nitrocellulose in a given solvent or solvent combination.[1]

Circulation of air during drying is maintained by means of a compressed air reservoir, and may enter the cylinder at either the top or bottom. The hot air preferably enters at the top so that the first heat is blown directly on to the cotton most completely dried, and then the heating is gradually extended across the length of the chamber to the cotton containing the greater proportion of moisture. At the end of five or six hours, the moisture content has been reduced to the minimum of 0.6%.

An alternative method of drying consists in placing cellulose in a large room on wire screens heated from below by means of a series of steam pipes, a slow current of air being aspirated under the shelves and through the cotton mass. As soon as the drying process has been completed, the heat is sometimes continued until the cotton is to be used, or, more usual, the cotton is removed, weighed out into batches and placed in air-tight containers as tin milk cans, where it is stored until ready for use. Cotton is always allowed to cool before nitration, although several methods have been proposed whereby the cellulose is immersed into the esterizing bath at a temperature equal to or greater than that of the acid bath. Less equipment is required to dry a given weight of

---

[1] H. Hofmann, Papier Ztg. 1906, **32**, 433, has called attention to the chemical change which sulfite cellulose and paper undergoes when being dried, which begins at a temperature of about 90°, and is dependent upon the temperature and time of heating. This change renders the cellulose more susceptible to attack by acids, but the sugar obtained by hydrolysis is the same (xylose). Straw, wood and rye are said not to be affected by drying at 100°.

FIG. 28.—SINGLE CONVEYOR DRYER VIEWED FROM DELIVERY END

cotton per unit length of time, where the cotton is taken out of the dry box as soon as dried and stored into air-tight receptacles until ready for use.

The drying process as carried out at Waltham Abbey, London, is as follows:[1] The cotton as it leaves the teasing machine is delivered on to an endless band which carries it to the drying machines. The cotton slowly passes through the machine, and issues at the end after about 45 minutes, with 0.5% moisture contained therein. The dry, hot cotton is then quickly weighed out into charges suitable for nitration, placed in sheet-iron boxes or other suitable receptacles with tight lids, and allowed to cool for about eight hours. During the cooling the moisture content of the cotton rises to about 1%, which is the amount of water contained in it, when it is plunged into the nitrating bath. During the passage of the fiber through the drying compartment, it is heated by a blast of hot air supplied by a fan or centrifugal blower, and warmed by a steam heater.

In some factories after the cotton has been dried, carbon dioxide gas from a cylinder is blown into the dry cotton until it is used. This practice is advantageous when the cotton drying units are situated close to the nitrating house, and the air may contain an appreciable amount of nitrous fumes.[2]

The A. Solod cotton dryer[3] comprises a rotary cylinder mounted on rolls in an inclined position, carriers at either end to feed and discharge the material into and out of the cylinder, and a perforated pipe in one side of the cylinder, through which heated air is forced from a hot air chamber.

In the B. Sturtevant method, the cotton is first passed through an opening machine or picker, then through an arrangement called by them the Empire Duplex Gin Company's C. O. B. machine. This process reduces the moisture content of ordinary staple cotton to about 2%. A small supplemental blower with

---

1. F. Nathan, J. S. C. I. 1909, **28**, 180.
2. Whereas a normal bone-dry cotton will average 0.4% nitrogen content when prepared for nitration, it has been found that when in close proximity to the nitrating house for some length of time, the nitrogen percentage will gradually rise to 0.8%-0.9%, and in heavy, foggy and rainy weather to as high as one per cent. It is claimed that cotton which has previously been charged with carbon dioxide nitrates more evenly and uniformly. This method of protecting dry cellulose has been used mainly in those factories producing nitrocellulose for artificial silk formation.
3. U. S. P. 1238589, 1917; abst. J. S. C. I. 1917, **36**, 1126.

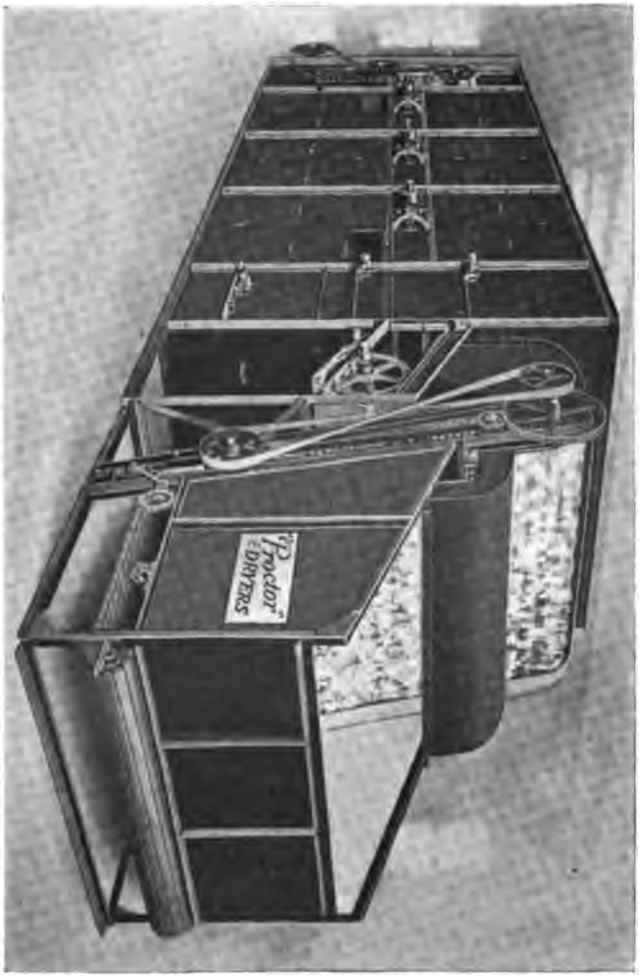


FIG. 29.—LOOKING AT THE FEED END OF "PROCTOR" THREE-CONVEYOR TYPE

heater finishes the drying process after the fiber has been placed in small bins. Thence it is handled as soon as dry by another blower which carries it to the nitrating plant.

The Proctor and Schwartz, Inc., of Philadelphia, Penna., have devized an automatic continuous system of drying. The apparatus is made of fire-proof material, is extensively used for this purpose, and is shown in detail in Figs. 26 to 31.

The apparatus is made of steel. The roofs of the dryers, as shown in illustrations, are insulated with asbestos and automatic fire-extinguishers located within the machine. Steam is used for heating, the coils being located in compartments at one side of each dryer, and the machinery parts may be either motor or engine driven. A mechanical conveyer system takes the moist cotton to the hoppers of the automatic feeds, located at the end of the dryers nearest to the teasers. Spiked feed aprons deposit the cotton in a uniform layer of the proper thickness on slowly moving conveyer screens. These carry it through the drying machines in about 30 minutes. During this time it is continuously subjected to the drying action of large volumes of moderately heated air in rapid circulation. Upon reaching the end of the machine in a uniformly dry condition the cotton either falls directly on the floor, into containers, or into a second hopper from which it is conveyed to any desired point.

In the "Proctor" automatic dryer system, the cotton is thrown into the hopper of an automatic feeder at the feed end of the machine. The feed automatically distributes the cotton on an endless conveyer which carries it through successive chambers graded from a moderately high heat at the feed end to a low temperature at the exit. Heated air is recirculated alternately through the material and the heating coils. In passing through the apparatus, the cotton is subjected to the opening action of rapidly revolving "kickers" or beaters. To this feature most of the efficiency of the machine, it is claimed, is due. Not only is uniform drying obtained, but the air-blast material assists in cleaning the cotton of dirt and grit which have resisted the earlier cleaning processes. The dirt falls to the floor and is removed through doors placed in the side of the dryer.

In their single conveyor type (Fig. 26), the dryer consists essentially of metal housings built up in sections on a structural steel framework. Fans for recirculating the warm air, steam coils for heating the air, exhaust for moist air and intake of dry air, and either one or three wire screen conveyors for carrying the cotton through the machine, are all located inside the housing. An automatic feeder is provided to evenly distribute the cotton in a thin uniform layer on the dryer conveyor.

The metal housing is made in sections so that it may be easily removed, or units added to increase the capacity. The dryer is divided into two compartments from end to end by a metal partition, one containing the steam coils and the other the conveyors. The fans are mounted on horizontal shafts and are located in the partition between the coil and conveyor chambers. The bearings of the fan shafts are all outside the enclosure, apart from the heat, and yet low enough to be reached from the floor. Fig. 28 shows the single conveyor dryer viewed from the delivery end.

The Proctor three-conveyor cotton dryer (Figs. 29, 30) is stated to be capable of handling two and one-half times as much cotton as a single conveyor dryer of the same length of main body, exclusive of the self-feed, and therefore is only recommended where large production is required. As the height of the three-conveyor dryer is considerably more than that of the single conveyor type, the height of room available will often be the determining factor.

The single and three-conveyor dryers operate on the same general principle, except that in the latter, the cotton is carried through the machine three times, and is dropped from one conveyor to another, twice. In the single conveyor type, the cotton passes through the housing but once. The units of both are made up in three widths, i. e., four, six, and nine feet. The length depends upon the number of units necessary to insure the capacity desired.

In Fig. 31 is shown in detail the interlocking sectional conveyor of the roller chain type used only in this form of cotton dryer, the individual sections of wire screen being 12 inches wide, and are bent over on the edges as shown. The sections interlock over a pipe which acts on the principle of a door hinge, the ends of the pipe fitting over studs on the roller chain on each side, while the ends of the screen are covered top and bottom by flanges on the chain. The figure shows a side view of the chain with two wire screen sections attached.

The manufacturers claim for this type of dryer—which has been used extensively in the United States for drying not only cotton, but a wide variety of products as well — the following points of superiority:

1. Economy in operation both in boiler house power, owing to the recirculation of air, and motive horse power owing to the large diameter of fans moving at comparatively slow speeds, and yet circulating the maximum amount of air.
2. The roller chain type conveyor, which *rolls*, not *drags*, through the dryer.
3. The pre-heating device on the delivery end of the dryers tends to cool the material coming from the conveyor, and at the same time warms the dry, fresh air which is being taken into the dryer.
4. The machine being substantially fire proof, and the absolutely *uniform* drying of the material on the conveyor from one side to the other, is of especial importance.

The method of Rosenberg[1] for drying in enclosed chambers consists of mechanical devices for regulating the entrance and exit of air, and was designed primarily for the drying of varnishes and resins.

Saco-Lowell Method of Cotton Preparation. The following description and illustrations (Figs. 32–36) indicate the general method of preparatory cotton treatment as devized and perfected by the Saco-Lowell Shops of Boston, Mass.

For cleaning the cotton or waste, a vertical opener with bale breaking feeder attached is employed, as indicated in Fig. 32, comprizing a heavy framework, each of the four sides and top being cast in one piece. Large clean-out doors are provided, also small doors at the bottom of sides for cleaning. The production is 6000–10000 pounds per 10 hours. The stock is run through this machine which delivers it into a pipe and can be conveyed by air to any desired location. At the end of this pipe is a condenser (Fig. 34) consisting of a screen with air passages from

---

[1] E. Rosenberg, E. P. 12070, 1913; abst. C. A. 1914, **8**, 3635; J. S. C. I. 1913, **32**, 1147. For the Norton apparatus for drying cotton previous to nitration, see Dingl. Poly. 1861, **160**, 428. The Semper method is described in Dingl. Poly. 1866, **180**, 344.

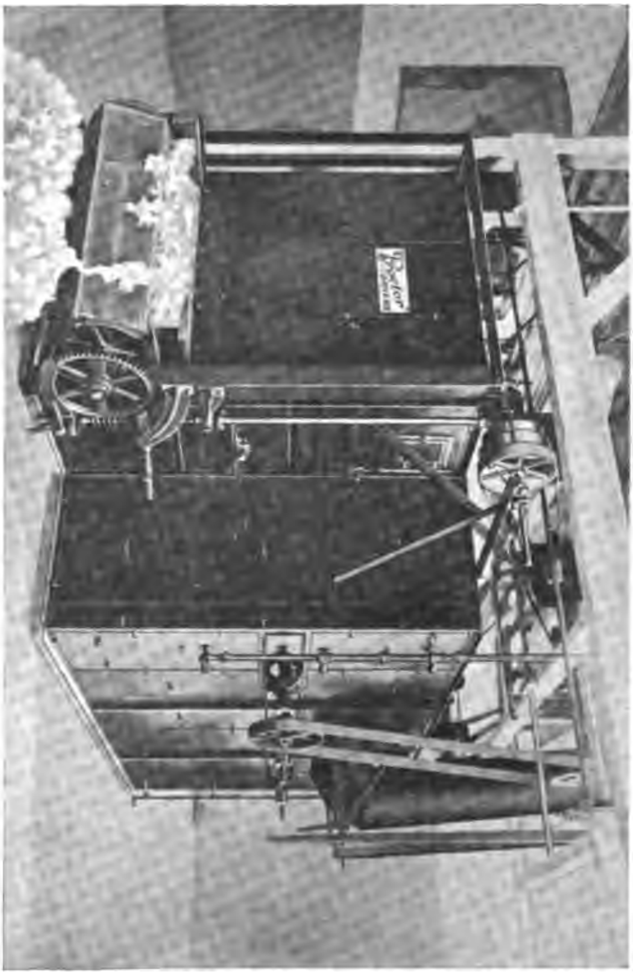


FIG. 30.—DRYING COTTON ON "PROCTOR" THREE-CONVEYOR DRYER (DELIVERY END)

each end, these passages being connected to a fan, as above described.

This fan draws the cotton from the vertical opener through a pipe to a screen on the condenser, the air, and dust, going through the condenser and fan blower into the separator. By this method the stock drops from the condenser screen into a bin, truck or machine, as desired. To provide additional cleaning, the stock is taken from bins and run through a breaker picker, as illustrated in Fig. 35, and from there to a finisher lapper (Fig. 36). The stock may be taken off in card form if desired, and then is in condition for boil-off and bleaching, preliminary to drying before nitration.

Treatment of Cotton for Esterification in Great Britain.[1] In the manufacture of nitrocotton, purified waste cotton from the spinning mills is mostly used, this material having been adopted by the Government many years ago. As the demand for the material increased, a special industry for its collection and treatment came into being in the cotton spinning districts. The raw waste is in a more or less dirty condition, the series of treatments to which it is subjected consists in freeing it from the various impurities picked up in the spinning mills, in order to leave, as far as possible, only normal resistant cellulose.

Formerly there was little connection between the cotton waste bleachers and the explosive manufacturers, the treatment of the waste being carried out by various firms each with a process of its own. The practice at this time was to buy to specification, but not to interfere with methods. The waste manufacturers had, of course, no knowledge of the effect of their processes on the resulting nitrocotton, and on the other hand, the explosive manufacturers were unfamiliar with the details of the treatment to which the waste was subjected.

With a colloidal body like cellulose, which cannot be purified by crystallization, it has come to be recognized that conformity to certain tests is not always indicative of purity or suitability for certain uses, it being desirable that the history of the material should also be known. An important step in the direction of

---

[1] For data contained in this topic, and elsewhere in this work, the author is indebted to Nobel's Explosives Company, their technical staff, and to Mr. F. W. Jones.

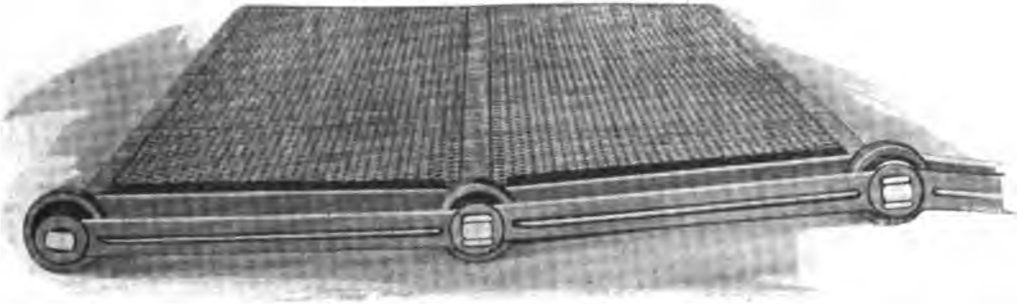


FIG. 31.—SIDE VIEW OF CHAIN CONVEYOR WITH TWO WIRE SCREEN SECTIONS ATTACHED

closer connection and greater chemical control was taken when Nobel's Explosives Company, some years ago, took over a mill and started waste manufacture on their own account. Various improvements and refinements were introduced by them—notably the omission of bleaching with chlorine, which had hitherto been considered an essential part of the treatment, but which is now recognized may produce harmful effects—were introduced, and have since found general application.

A further progessive step towards standardization of processes became possible during the recent war when Government control of all munitions became necessary, and the Waste Mills were taken over by the Ministry of Munitions. Considerable work was carried out by the Department in conjunction with the explosives manufacturers in the direction of arriving at the most suitable and expeditious purification treatment.

Although cotton waste comprizes a wide range of materials, this waste material as used in Great Britain may be divided into the following three classes:

(1) Waste from the ginning operations usually carried out on the plantations. This includes short fiber material like linters and wadding, and also a very low grade material known as hull fiber, which remains attached to the seeds after the removal of the linters.

(2) Waste from the spinning mills, including mill sweepings, and also a certain proportion of refuse from the preliminary cleaning operations known as flocks, scutchings, etc.

(3) Waste from the weaving mills.

As above mentioned, the materials generally employed are spinning mill sweepings, wadding known as old China wadding, the latter being used to a minor extent, and imported from China, where it is employed for padding and quilting clothing, chiefly in Manchuria and the colder regions. The length of individual fiber of this material is quite satisfactory.

Linters, although largely used in the United States and Europe, have not been used to any great extent in England. Hull fiber contains a very large proportion of husks and woody matter, and is, therefore, unsuitable unless submitted to improved

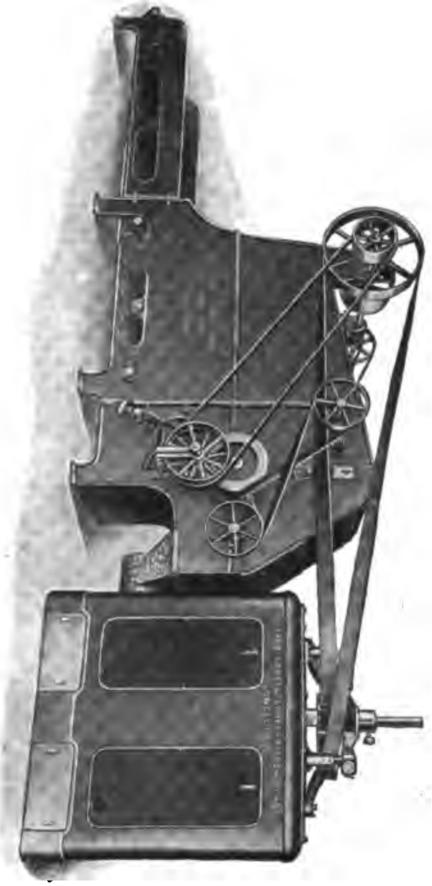


FIG. 32.—COTTON BALE BREAKER ATTACHED TO VERTICAL OPENER

methods of purification. In the F. Stockton process[1] the fiber separated from cottonseed hulls is purified by boiling in a 4% aqueous solution of a caustic alkali for about 5 hours to soften the hull particles, mashing and disintegrating the latter by passing the material between rolls, and then subjecting the mashed mixture to a cleaning operation to separate the fiber from the disintegrated hull material.[2]

Weaving mill waste, although otherwise excellent material consisting of high grade cotton, is liable to contain starch which is used in the mills to strengthen the fiber during weaving, and as nitrostarch with its diminished stability may be formed in nitration, the use of this material is not permitted by the British Government, whose standard of stability is of an exacting nature. Dyed material has also been found unsuitable.

Spinning mill sweepings consist of good unspun cotton of long staple and almost husk-free, being only discarded in the mill as inevitable waste, and not on account of defects in the fiber. It contains a variable amount of spun cotton, as well as considerable (15%-25%) lubricating oil from the machinery, other impurities consisting of pieces of wood, metal, string, paper, and sandy matter picked up from the mill floor.

China wadding is unspun material, felted and somewhat discolored, but usually clean material. It contains no oil, and deoiling treatment is, therefore, not required.

The general treatment consists in removing the mechanical impurities by hand picking and treatment in dusting machines, the solvent extraction of the oil, boiling under pressure with dilute sodium hydroxide solution, washing, centrifugalizing to remove water, drying, and further treatment in teasing and willowing to open out the material and remove foreign matter. The finished waste is then weighed and press packed into bales for transit to the Explosives Factories.

For hand picking wire gauze tables are used to allow the fine refuse to fall out, the material being then passed through a

---

[1] U. S. P. 1295078, 1919; abst. C. A. 1919, **13**, 1156; J. S. C. I. 1919, **38**, 319-A. E. P. 132422.

[2] Ordinarily, second cut linters has a maximum length of about 25 mm., a minimum of 0.8 mm., and an average of about 4.6 mm. Hull shavings will average about 2.4 mm. with a maximum of 8 mm., depending on how much linters have been removed from the seeds, and a minimum of 0.5 mm.

FIG. 33.—FEEDER ATTACHED TO VERTICAL COTTON OPENER

long revolving sieve in which detritus is further removed, and is then loaded into large spherical revolving kiers in which the de-oiling takes place. Formerly benzine was used for this purpose, but has now been replaced by trichloroethylene (Westrosol), which being non-inflammable, is much safer. When the oil has been extracted by successive extractions with solvent, the residual solvent is expelled by means of steam and recovered. The mass at this stage has considerably contracted, and material which requires no de-oiling is now added, and treatment with alkaline solution given. The strength of the solution, the pressure and time of treatment are carefully coördinated, depending on the type of cotton required. Special care is taken not to expose the material to the air while it is in contact with alkali to avoid oxidation.

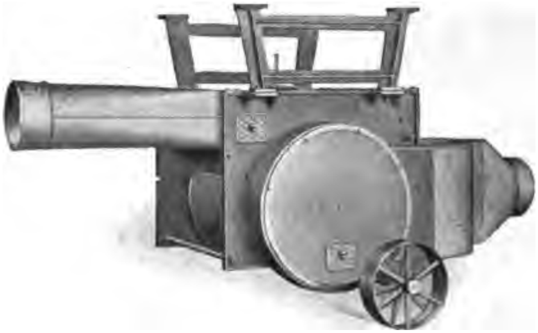


FIG. 34.—SACO-LOWELL CONDENSER

The cotton having been discharged from the kier, is washed in a paddle washing machine in which it is kept in constant motion, fresh water being continuously admitted and removed by means of a gauze drum. The cotton is then removed from the washer by means of an endless belt conveyor, and wrung in centrifugal machines until the moisture content is reduced to about 45%, after which it is passed through an opening machine consisting essentially of revolving spiked rollers, preparatory to the final drying.

For this purpose a Petrie drying machine of large size is generally used, the machine consisting of a chamber filled with

FIG. 35.—ONE-BEATER COTTON BREAKER WITH FEEDER.

moving shelves, arranged one above the other, over which a current of hot air from a fan and tubular heater is passed. The cotton is fed into the top of the machine by means of a belt conveyor, and by a special motion, slowly passes along each shelf until it is delivered at the bottom in a sufficiently dried condition. The time taken for the cotton to pass through the machine is about one hour, and the moisture content has then been reduced to about 7%—the amount usually present in air dry cotton.

The cotton is now passed through the willowing machine in which a rotating drum fitted with blunt spikes beats it against a grating, small pieces of wood, sand, and other mechanical impurities being in this way removed. From the willowing machine the cotton passes to a teasing machine, consisting essentially of an arrangement of spiked rollers, which uniformly opens out the stock. It is then again hand picked (see Fig. 37), and is finally weighed off and press packed into bales for despatch.

The cotton was formerly subjected to bleaching with chlorine and souring with weak acid, but these treatments are now omitted, as they are considered unnecessary, and may in addition lead to the formation of oxycellulose and hydrocellulose.

In the manufacture of those explosives and products of lower nitration in which a solvent is required, it is of importance from the economic standpoint that the minimum of solvent be used, and the nitrocotton, therefore, should have a low viscosity. Much attention, therefore, has been given to lowering the viscosity of the cotton, as this is intimately related to the viscosity of the nitric ester formed therefrom, and a somewhat drastic treatment is given.

For nitrocotton for blasting gelatin and other blasting explosives on the other hand, a high viscosity is desired, and the treatment indicated in this case, therefore, is much less drastic. It has been proposed to purify the cotton by means of alcoholic sodium hydroxide solution, but this is unduly expensive. The nitration of squirted dissolved cotton has also been proposed,[1] but has not been adopted in manufacture.

Due to the rapid deterioration owing to the action of bacteria, cotton should not be stored in a damp condition. Wet

---

[1] Ball's "Nature," 1915, **7**, 15.

Fig. 36.—Intermediate or Finisher Lapper for Cotton

purified cotton containing 15%–20% of moisture has been found to develop a temperature of 60°, when stored under conditions which prevented free access of air (see p. 338). The number of bacteria rapidly multiplies when the moisture content exceeds 9%, and it is a difficult matter to destroy them—an exposure for one to two hours at a temperature of 150°–160° being required.

The examination of the finished cotton waste includes the estimation of moisture, which should not exceed 7%, ether extract (oil), 0.6%; solution in 3% NaOH solution (1 vol. to 2 vols. water), after 15 minutes heating at 100°, 1%; calcium oxide and other mineral matter, 1.25%.

Application of a basic dyestuff as fuchsine should not show deeply dyed particles or fibers, and the viscosity of the solution in Schweizer's reagent should also be determined.

In the preparation of the cotton for nitration, as the stock arrives at the Explosives Factories in bale form, it is necessary to open it out before nitration in order to insure uniform penetration of the cotton by the nitrating mixture. The moisture content is also reduced as far as possible to obviate the weakening of the acid, and make the nitrating process better controllable. While it is advantageous that all cleaning treatment, so far as possible, be carried out at the waste mills, but as a further precaution the explosives manufacturers usually give an additional treatment with the object of removing mechanical impurities, such as sand and small pieces of woody matter still present in the cotton.

The general line of treatment consists in opening up the bale of cotton, teasing, drying, willowing, or dusting to eliminate foreign matter, and weighing off for nitration. The cotton was at one time also hand picked, but improved treatment at the waste mills has made this superfluous. For this purpose wire gauze tables were used, which allowed sand and other extraneous particles to fall out, as shown in Fig. 38.

After passing through the teasing machine similar to that described under the preliminary purification, and then through a drying machine (see Fig. 39), in which the moisture is reduced to about 1%, the cotton is passed through a willower, or in a dusting machine consisting of a revolving sieve in which foreign matter is removed, and is finally weighed off into sheet iron

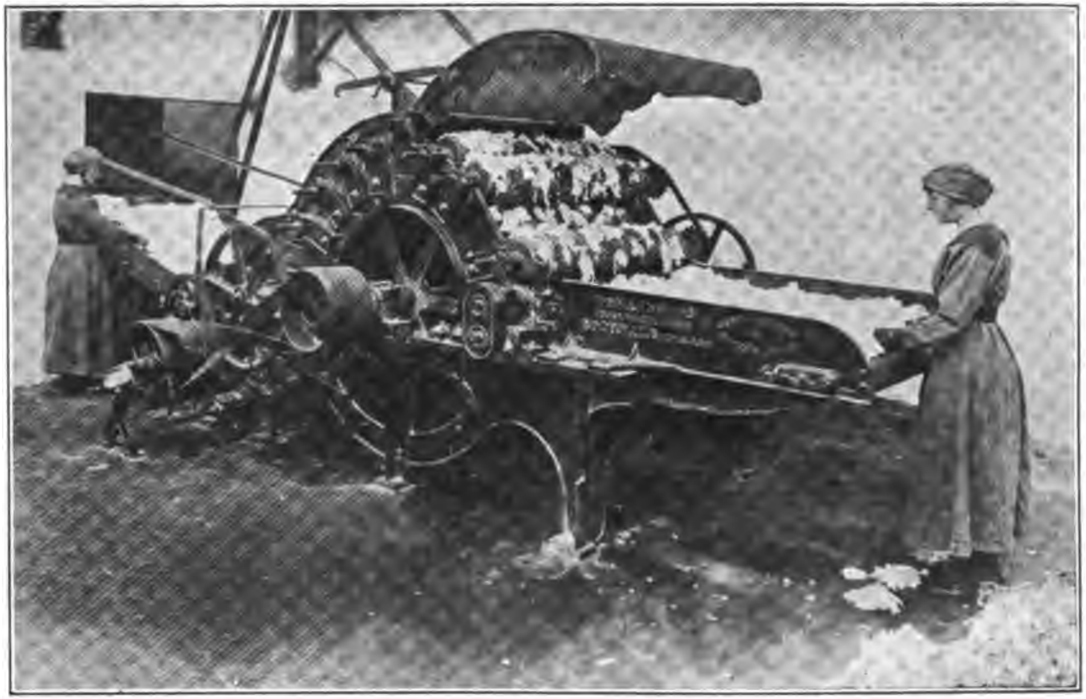


Fig. 37.—Cotton Teasing (Nobel's Explosives Co.)

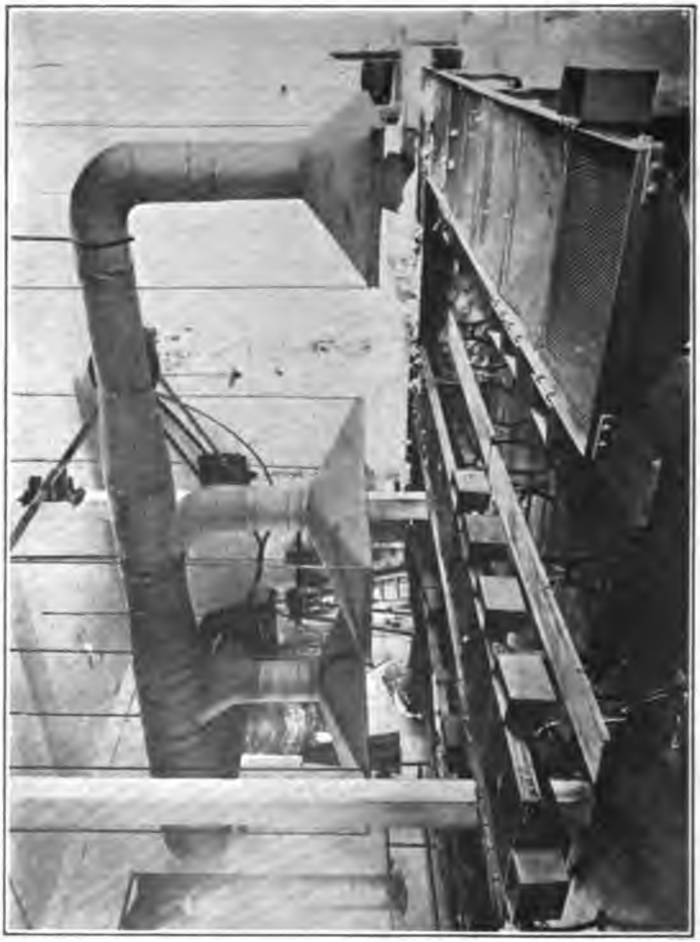


Fig. 38.—Hand Picking of Cotton for Nitration (Nobel's Explosives Co.)

boxes with tightly fitting lids, where it is allowed to cool for several hours before nitration.

The machines are arranged in series and are fitted with draught hoods connected to an exhaust fan for the removal of fluff and dust. The exhaust from the fan is led into a dust collector known as a "cyclone," consisting of an inverted cone, round which the air circulates (see Fig. 40). The friction of the air on the sides causes the fluff to be deposited and to fall to the bottom, where it drops into a suitable receptacle, while the air escapes at the top.

In preparing cotton for nitration, it is essential that it should be well opened to ensure uniform and complete acid penetration, as defective opening lowers the nitrogen content, and raises the solubility of the resulting nitrocotton.[1] This is an important

[1] A. Classen, U. S. P. 647805, 654518, 1900; Re. 12069, 1902; 695795, 1902; 825808, 1906. C. Cross, U. S. P. 807250, 1905. M. Ewen and G. Tomlinson, U. S. P. 763472, 1904; India Appl. 470, 1909. P. Ekström, Swed. P. 33546; Hung. Anm. E-1796; abst. Chem. Ztg. 1913, **37,** 11, 163. R. Eisentraut, E. P. 1443, 1887. Elektro-Osmose, D. R. P. 296053, 305118, 1917; abst. J. S. C. I. 1917, **36,** 593; 1920, **39,** 60-A. S. Eraly, A. Christiansen, The Farringdon Works, Ltd., and H. Pontifex & Sons, E. P. 3602, 1911; F. P. 429934; abst. C. A. 1912, **6,** 2022; J. S. C. I. 1911, **30,** 1301; 1912, **31,** 218. A. Fest, Can. P. 173954, 1916. E. Fischer, Ber. 1916, **40,** 584; abst. C. A. 1916, **10,** 1532. E. Fischer and H. Noth, Ber. 1918, **51,** 321; abst. C. A. 1918, **11,** 2558; J. C. S. 1918, **114,** i, 225. See C. A. 1917, **10,** 1040. F. Fischer and W. Schneider, Ges. Abhandl. Kenntn. Kohle, 1919, **3,** 287; abst. Chem. Zentr. 1919, **90,** III, 287; abst. J. S. C. I. 1920, **39,** 225-A. F. Fischer and M. Kleinstück, Ges. Abhandl. Kenntn. Kohle, 1919, **3,** 301; Chem. Zentr. 1919, **90,** IV, 940. J. Flack, Can. P. 183164, 1918. Gewerkschaft Pionier, F. P. 415566, 1910. Glanzfäden Actiengesellschaft, D. R. P. Anm. F-26697; abst. Chem. Ztg. 1913, **37,** 387. W. Glover, U. S. P. 828472, 1906. W. Glover and L. Wilson, U. S. P. 1279329, 1918. M. Gostling, Proc. Chem. Soc. 1902, 250. H. Grothe, Dingl. Poly. 1870, **196,** 553; abst. Poly. Centr. 1870, **36,** 641. E. Hägglund, Ark. Kemi. Min. och Geol. 1918, **7,** 1; abst. Chem. Zentr. 1919, **90,** III, 186; J. S. C. I. 1919, **38,** 895-A. T. Hanausek, Chem. Ztg. 1894, **18,** 441. Holzstoffwerke Brixem-Pfeffersberg Otto Kurz A. G., Aust. P. Anm. 10723, 1911; abst. Chem. Ztg. 1913, **37,** 254. C. Hoepfner, U. S. P. 663759, 1900. M. Hönig and J. Spitzer, Monatsh. Chem. 1918, **39,** 1; abst. J. C. S. 1918, **114,** i, 375; J. S. C. I. 1918, **37,** 502-A. C. Hudson, J. A. C. S. 1915, **37,** 1591; J. Ind. Eng. Chem. 1916, **8,** 380; C. A. 1915, **9,** 2092; 1916, **10,** 1501. C. Hudson and D. Brauns, J. A. C. S. 1915, **37,** 1283; J. C. S. 1915, **108,** i, 320, 502; C. A. 1915, **9,** 1771. C. Hudson and J. Dale, J. A. C. S. 1915, **37,** 1280; 1918, **40,** 992, 997; C. A. 1915, **9,** 1771; 1918, **12,** 1778; J. C. S. 1915, **108,** i, 502. C. Hudson and J. Johnson, J. A. C. S. 1915, **37,** 1270, 1276; abst. C. A. 1915 **9,** 1770; J. C. S. 1915, **108,** i, 502, 503. C. Hudson and H. Parker, J. A. C. S. 1915, **37,** 1598; abst. C. A. 1915, **9,** 2092. International Cellulose Co., Can. P. 176178, 1917. G. Jenssen, Can. P. 180612, 1917. A. Jernberg, Can. P. 181513, 1918. F. Jaeger, Proc. Acad. Sci. Amsterdam, 1917, **20,** 280; abst. C. A. 1918, **11,** 1047. C. Kellner, U. S. P. 773941, 1904; E. P. 5420, 1890. I. Kitsee, U. S. P. 703135, 1902; 767822, 1904. J. König and E. Becker, Pap. Fabr. 1919, **17,** 982, 1014, 1171; abst. C. A. 1920, **14,** 626.

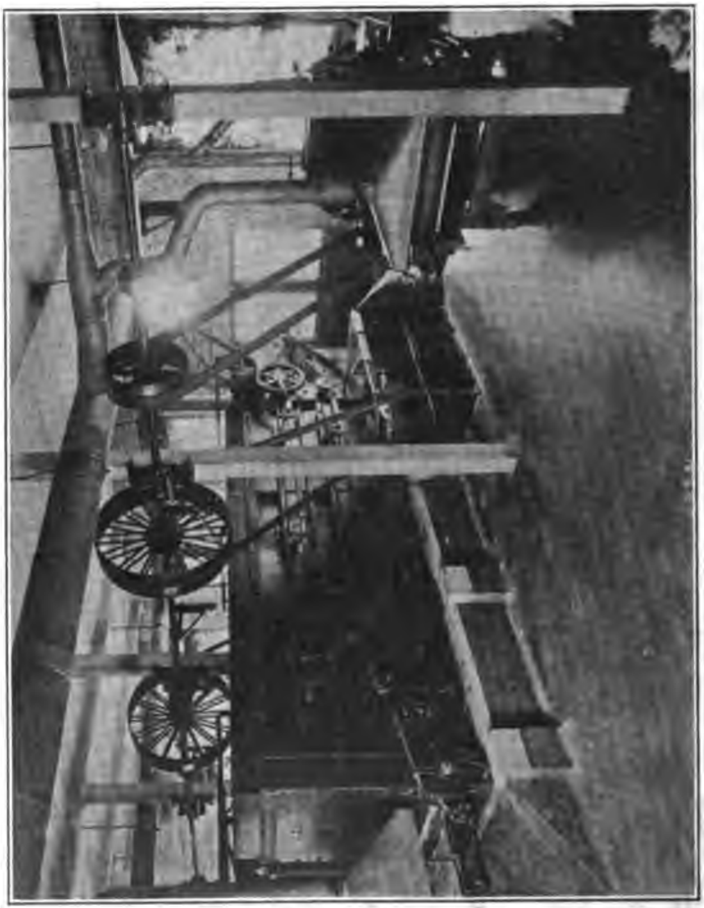


FIG. 39.—COTTON DRYING MACHINE (NOBEL'S EXPLOSIVES CO.)

FIG. 40.—CYCLONE DUST COLLECTOR (NOBEL'S EXPLOSIVES CO.)

point which has not been given the consideration that it should. W. Koenigs and E. Knorr, Ber. 1901, **34**, 4343; abst. J. S. C. I. 1902, **21**, 196. H. Kunz-Krause and R. Richter, Arch. Pharm. 1917, **255**, 507; abst. J. C. S. 1919, **116**, ii, 436; C. A. 1920, **14**, 796. H. Lange, Farber Ztg. **7**, 441. W. Lawrence, Can. Chem. J. 1919, **3**, 329; abst. C. A. 1920, **14**, 127. J. Leonard, U. S. P. 237440, 1881. A. Lietzenmayer, Swiss P. 58688; abst. Chem. Ztg. 1913, **37**, 284. J. London and H. Bailey, E. P. 12711, 1895. E. Masera, Ital. P. 385/141/125268; abst. Chem. Ztg. 1913, **37**, 272. W. Mather, J. Hübner and W. Pope, U. S. P. 824255, 1906. T. McFarland, U. S. P. 858411, 1907. R. McKee, U. S. P. 1284739, 1284740, 1918; abst. J. S. C. I. 1919, **38**, 71-A; C. A. 1918, **13**, 186, 187. P. Menaul and C. Dowell, J. Ind. Eng. Chem. 1919, **11**, 1024; abst. C. A. 1920, **14**, 258. W. Mensing, D. R. P. 304349; abst. J. S. C. I. 1920, **39**, 274-A. P. Minck, U. S. P. 1317306, 1919; abst. J. S. C. I. 1920, **39**, 103-A. J. Minor, Paper, 1919, **25**, 700; abst. C. A. 1920, **14**, 344. M. Moore, Can. P. 153445, 1914. H. Morrow, E. P. 9319, 1885. M. Murai, D. R. P. 257609; abst. Chem. Ztg. 1913, **37**, 245. H. Nastukoff, Ber. 1900, **33**, 2237; abst. J. S. C. I. 1900, **19**, 733. A. Neilson, Can. P. 197280, 1920. A. Nodon, Can. P. 154820, 1914; Belg. P. 253427, Chem. Ztg. 1913, **37**, 397. Z. Ostenberg, U. S. P. 1315393, 1919; abst. J. S. C. I. 1919, **38**, 897-A. A. Pellerin, Can. P. 148405, 1913. L. Peufaillit, Can. P. 150817, 1913. M. Petzold, Aust. 57989; abst. Chem. Ztg. 1913, **37**, 262. M. Pomeranz, Chem. Ztg. 1918, **42**, 177; Chem. Zentr. 1918, **89**, II, 227; C. A. 1920, **14**, 353. Haller, Chem. Ztg. 1917, **41**, 852. D. Porter, E. P. 8184, 1909. H. Pringsheim and H. Magnus, Zts. ang. Chem. 1920, **33**, 56; abst. J. S. C. I. 1920, **39**, 266-A. M. Platsch, Hung. Anm. P-3702, 1912; abst. Chem. Ztg. 1913, **37**, 272. W. Quist, Pap. Fabr. 1919, **17**, 818; abst. C. A. 1920, **14**, 344. H. Riesenfeld and F. Taurke, Proc. Amer. Pharm. Assoc. 1906, **54**, 909; Chem. News, 1905, 201; Ber. 1905, **38**, 12. E. Rinman, E. P. 8175, 1909; 6652, 1912; Can. P. 168362, 180925, 1917. D. Rosenblum, L. Brech and E. Tyborowski, D. R. P. 252321, 257544; Hung. Anm. 3134; abst. Chem. Ztg. 1913, **37**, 245, 272. L. Brech, Can. P. 145860, 1913. E. Savery, Dingl. Poly. 1879, **231**, 558; abst. Jahr. Chem. 1879, **32**, 1152. W. Schach, D. R. P. 306366, 1918; abst. J. S. C. I. 1920, **39**, 60-A. E. Schauffelberger, U. S. P. 1282835, 1918; Can. P. 187949, 1918. F. Schreyer, Can. P. 141089; Aust. P. 58102; abst. Chem. Ztg. 1913, **37**, 272. C. Schwalbe, F. P. 410460, 1910; Can. P. 141034, 1912. Zts. ang. Chem. 1919, **32**, 355; abst. J. S. C. I. 1920, **39**, 58-A. See also J. S. C. I. 1919, **38**, 858-A. C. Schwalbe and E. Becker, Zts. ang. Chem. 1919, **32**, I, 265; abst. C. A. 1920, **14**, 837. E. Simonsen, U. S. P. 607091, 1898. Soc. anon. La Soie Artificielle, F. P. 477655, 1915; Ital. P. 385/185 125107; abst. Chem. Ztg. 1913, **37**, 284. A. Pictet, Can. P. 195897, 1920. S. Lagermarck, Can. P. 162481, 1915. I. Soraas, Can. P. 196329, 1920. Peter Spence and Sons, Ltd., Belg. P. 250441; abst. Kunst. 1913, **3**, 235. O. Stafford, Can. P. 182877, 1918. O. Stage, U. S. P. 1279604, 1918; Can. P. 187316, 1918. R. Sthamer, U. S. P. 692497, 1902; D. R. P. 123121; abst. Chem. Zentr. 1901, **72**, II, 567. H. Stockbridge, Paper, **22**, No. 11; C. A. 1913, **7**, 2305; 1917, **11**, 1299. R. Strehlenert, Can. P. 151445, 1913. F. Taylor, E. P. 10864, 1884. C. Thorne, Can. P. 153694, 1914. G. Tomlinson, Can. P. 182387, 1918. C. Vanderkleed and J. Brewer, U. S. P. 1269340, 1918. T. Wagner, U. S. P. 1261328, 1918; Can. P. 186713, 1918. E. Wallin, Swed. P. 43761, 1918; abst. C. A. 1919, **13**, 251. R. v. Walther, D. R. Anm. 38809; abst. Chem. Ztg. 1913, **37**, 379. A. Westad and E. Hägg, Can. P. 195943, 1920. H. Wichelhaus, Ber. 1919, **52**, 2054; abst. J. S. C. I. 1920, **39**, 59-A. See also J. S. C. I. 1916, **35**, 1151; 1918, **37**, 120-A. A. Wilbaux, E. P. 17268, 1890. J. Williams, E. P. 1358, 1898. E. Winterstein, Zts. Physiol. Chem. **17**, 391; J. C. S. 1893, **64**, i, 127. Zellstoff-fabrik Waldhof, E. P. 132815, 1917; abst. J. S. C. I. 1920, **39**, 14-A; C. A. 1920, **14**, 346. D. R. P. 304214, 1916. Norw. P. 29748, 29763, 1919; abst. C. A. 1920, **14**, 1219; J. S. C. I. 1920,

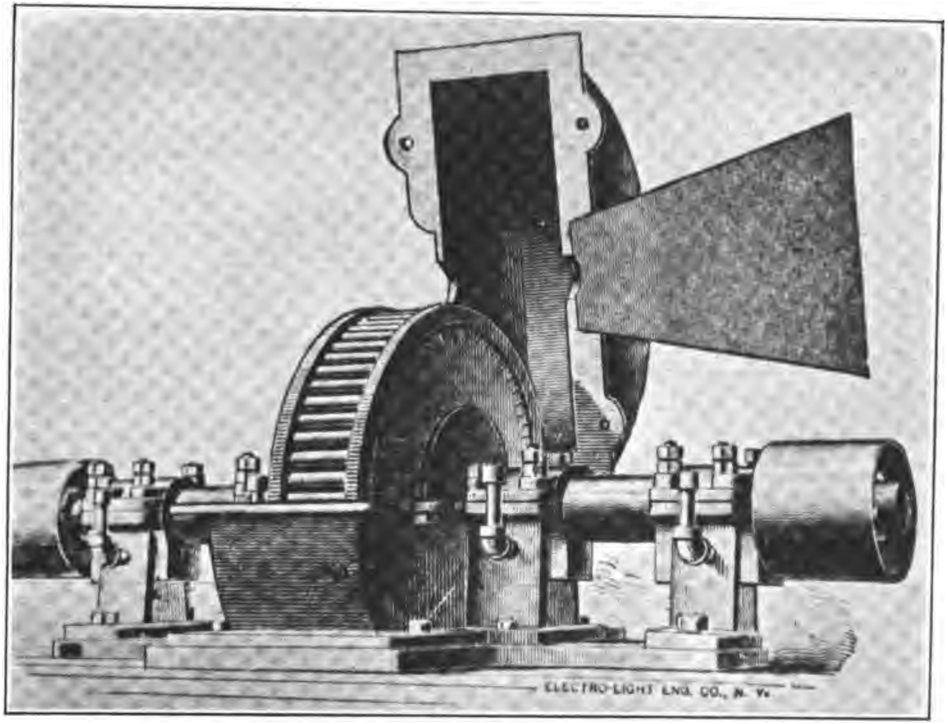
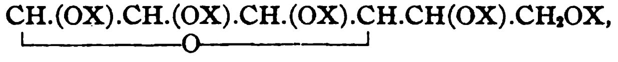


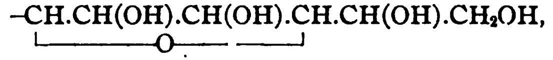
FIG. 41.—COTTON DISINTEGRATOR

K. Hess[1] has recently contributed an important paper on the consitution of cellulose in which it is suggested that the molecule of hydrocellulose, for which the name celluxose is now suggested, consists of a dextrose or a cellobiose molecule in which the hydroxyl groups are etherified by dextrose or cellobiose residues. Of the various possibilities, the formula



$$\underbrace{\mathrm{CH.(OX).CH.(OX).CH.(OX).CH}}_{\mathrm{O}}\mathrm{.CH(OX).CH_2OX,}$$

in which X represents the residue



$$-\underbrace{\mathrm{CH.CH(OH).CH(OH).CH}}_{\mathrm{O}}\mathrm{.CH(OH).CH_2OH,}$$

is in closest agreement with the proportions of cellobiose acetate (6.2 gm.) and pentacetyldextrose (12 gm.) obtained from cellulose (10 gm.) by acetolysis. The dextrins, which are present in the form of acetates when the maximum proportion of cellobiose acetate is not reached, are looked on as mixed partial degradation products of the cellulose molecule, resulting from the removal by hydrolysis in a variety of ways of one or more dextrose or cellobiose residues. Experiments on the acetolysis under very mild conditions of ethylcellulose uniformly confirmed the deduction from the above formula that when degradation has proceeded sufficiently far, the ethoxy number of the ethyldextrin acetates produced should be less than that of the ethyldextrose; this result is not explained by the older formulas. The marked difference between cellulose and its derivatives, e. g., nitrate, acetate, and the products obtained by the action of acids, alkalis, or zinc or copper ammonium compounds is accounted for by con-

---

39, 60-A. G. Zemplen and E. Laszlo, Ber. 1915, **48,** 915; abst. Chem. Zentr. 1915, **86,** II, 123.

P. Bettinger, Bull. assoc. chim. sucr. dist. 1919, **37,** 126; abst. C. A. 1920, **14,** 1235. A. Claessen, U. S. P. 602697, 1898. J. David, U. S. P. 769061, 1904. J. Kantorowicz, U. S. P. 785216, 1905. H. Pomeranz, Drog. Ztg. 1919, 236; Pharm. Zentralhall. 1918, **60,** 510; C. A. 1919, **13,** 521, 915; 1920, **14,** 1235. G. Raynaud, U. S. P. 761542, 1904. J. Bolling, U. S. P. 1305518, 1919; abst. C. A. 1919, **13,** 1961. R. Kadish and T. Buscher, U. S. P. 1327394, 1920; abst. J. S. C. I. 1920, **39,** 228-A. I. Meunier, Rev. Sci. 1919, **57,** 135; abst. C. A. 1919, **13,** 1255. E. Rasser, Papfabr. 1918, **16,** 274; abst. C. A. 1919, **13,** 2595. R. Weiss, Bull. Soc. Ind. Mulh. 1914, **84,** 499; (Sealed communications deposited May 28 and June 23, 1902.) A. Berglind, U. S. P. 1329824, 1920. J. Bland and E. Gelligan, U. S. P. 739751, 1903. J. Cochran, U. S. P. 822430, 822883, 1906. R. Van Buggenboudt, U. S. P. 872097, 1907. D. Winn, U. S. P. 739246, 1903.

[1] Zts. Elektrochem. 1920, **26,** 232; abst. J. S. C. I. 1920, **39,** 232. See also H. Ost, Zts. ang. Chem. 1906, **19,** 993; abst. J. S. C. I. 1906, **25,** 606.

sidering such derivatives to be derived from the above formula, while cellulose consists of a number of such molecules, united through residual affinities of hydroxyl groups. The disintegrating effect of the agents named is due to their competition for these residual valencies. It is also suggested that the physical characteristic of cellulose as a hollow fiber is reproduced in the arrangement of the celluxose molecules in the cellulose complex, and that this complex may be broken down by mechanical means.

In continuing his researches on lignin, P. Klason[1] has come to the conclusion that a hypothetical coniferyl aldehyde and coniferyl alcohol are the most important and sole chemically active constituents of coniferous lignin. E. Knecht and F. Fernandes[2] have recorded tables showing the percentage of matter extracted from Egyptian and American cotton by different solvents, the effect of heat on the extracts, and their nitrogen content.

The heat of combustion of absorbent cotton has recently[3] been determined as 4020 cal. per gm. W. Qvist[4] has determined the alkalinity of various samples of cellulose, using an ether solution of iodeosine as indicator, hydrocellulose and oxycellulose showing an acidic reaction which became alkaline on washing, while cellulose and especially oxycellulose, could absorb both acids and alkalis from solutions. C. Schwalbe and E. Becker[5] have found a variety of cellulose which is practically without reducing power, and is obtained by the action of boiling milk of lime on all sulfite celluloses, hydro- and oxy-celluloses. The gas mantle of the Deutsche Gasglühlicht A.-G.[6] is composed of hydrocellulose.

[1] Ber. 1920, **53**, B, 706; abst. J. C. S. 1920, **118**, i, 474.

[2] J. Soc. Dyers Col. 1920, **36**, 43; abst. J. S. C. I. 1920, **39**, 481-A. Cf. E. Knecht, Text. Inst. J. 1911, **2**, 22; abst. J. S. C. I. 1911, **30**, 1007. E. Knecht and W. Hall, J. Soc. Dyers Col. 1918, **34**, 220; abst. J. S. C. I. 1919, **38**, 7-A.

[3] T. Richards and H. Davis, J. A. C. S. 1920, **42**, 1608.

[4] Pulp and Paper Mag. 1920, **18**, 261, 285; abst. J. S. C. I. 1920, **39**, 443-A.

[5] J. prakt. Chem. 1919, (2), **100**, 19; abst. J. C. S. 1920, **118**, i, 474; C. A. 1920, **14**, 2081. See also Zts. ang. Chem. 1920, **33**, 57, 58; abst. J. S. C. I. 1920, **39**, 330-A. C. Schwalbe, Zts. ang. Chem. 1919, **32**, I, 355; abst. C. A. 1920, **14**, 1437. Further contributions to the chemistry of cellulose have been made by F. Fischer and W. Schneider, Ges. Abhandl. Kenntn. Kohle, 1919, **3**, 287; abst. C. A. 1920, **14**, 2081. F. Barret, J. S. C. I. 1920, **39**, 81-T; abst. C. A. 1920, **14**, 1757. E. Heusef, Chem. Ztg. 1915, **39**, 89, 141, 170.

[6] D. R. P. 312577, 1918; abst. J. S. C. I. 1920, **39**, 441-A.