THE PAPER MILL CHEMIST

H. P. STEVENS, M.A.

SECOND REVISED EDITION

10/6

THE PAPER MILL CHEMIST

BY

HENRY P. STEVENS, M.A., F.I.C.

CONSULTING CHEMIST TO THE PULP AND PAPER TRADES

SECOND REVISED AND ENLARGED EDITION

WITH 67 ILLUSTRATIONS AND 82 TABLES

LONDON
SCOTT, GREENWOOD & SON
8 BROADWAY, LUDGATE, E.C. 4
1919

NEW YORK
D. VAN NOSTRAND COMPANY
EIGHT WARREN STREET

First Edition 1908
Second Edition, Revised and Enlarged, May, 1919

PRINTED IN GREAT BRITAIN
BY THE ABERDEEN UNIVERSITY
PRESS LTD., ABERDEEN.

PREFACE TO THE FIRST EDITION.

THIS book has been written with the object of providing in a handy form the necessary information for carrying out chemical and physical tests on paper and the raw materials used in its manufacture, and to supply in a convenient form those analytical and practical papermaking data which may be useful for purposes of reference.

With this end in view I have incorporated a large number of tables and a fairly complete index, as well as a number of cross references in the text. Some of the tables have been recalculated, and great pains have been taken to check the numerous data and insure accuracy.

The book has been printed in handy pocket form, and it is hoped that it will be of service to all those engaged in practical papermaking, as well as to analysts, stationers, and others who test and examine papers.

I have great pleasure in acknowledging the help afforded me by my colleague, Mr. Clayton Beadle, who has read the proofs and made numerous and valuable suggestions.

HENRY P. STEVENS.

LABORATORIES, 15 BOROUGH,
LONDON BRIDGE, S.E. 1, *November*, 1907.

PREFACE TO THE SECOND REVISED EDITION.

The general arrangement and scope of the book have been retained, but the whole subject-matter has been revised and brought up to date by rewriting parts of the text dealing with recently published experimental work.

I am indebted to those who have called my attention to misprints and other errors in the original Edition.

H. P. S.

London, *April*, 1919.

CONTENTS.

CHAPTER I.

CHAPTER II.

CHAPTER III.

CHAPTER IV.

CHAPTER V.

CHAPTER VI.

Cellulose and the Isolation of Paper-making Fibres—Examination and Properties of Rags and Rag Liquors—Rag Boiling—Nature and Examination of Pulp Woods—Production and Yields of Mechanical, Sulphite and Sulphate Pulps—Examination of Sulphite Liquors and Gases—Production and Yields of Straw, Esparto, Bamboo and other Pulps—Soda Recovery—Ammonia Process for Production of Cellulose—Examination of Cellulose and Half-stuffs—Bleaching Fibres—Beating—Colouring Pulp and the Application of Coal-tar Colours—Estimation of Moisture in Pulp.

CHAPTER VII.

Microscopic Examination and Identification of Fibres—Microscopic Characteristics of Cotton, Linen, Hemp, Manila, Jute, Esparto, Straw, Ramie, Bamboo, and Wood Fibres—Determination of Percentage Composition of Furnish—Reagents for Staining Fibres.

Paper Testing—Thickness—Bulk—C. B. and S. Units—Distribution of Fibres—Tensile Strength and Elongation—Resistance to Wear and Tear—Sizing Qualities.

Blotting Papers—Absorbency—Zone Tests—Permeability of Filter Papers.

Chemical Analysis of Paper—Percentage of Composition of Loading—Nature and Proportion of Size—Spots and Specks in Paper—Chemical Impurities in Paper.

CHAPTER VIII.

Paper Scales—List of Sizes—Conversion of Ream Weight to Metric Units and *vice versâ*.

CHAPTER IX.

Contract Note for Wood Pulp—Paper Trade Customs in Great Britain and Ireland—Canadian Trade Customs—Trade Customs of the Book Mills in U.S.A.

LIST OF TABLES.

CHAPTER I.

ENGLISH AND METRICAL SYSTEMS OF WEIGHTS AND MEASURES.

THE system of weights and measures commonly in use in the mill, in which weights are expressed as pounds, qrs., cwts., and tons, and volumes in gallons, is not that adopted in chemical work. It is found more convenient to use a metrical system in which all quantities are expressed in multiples or fractions of the unit. Thus, the unit of weight being 1 gram (or gramme), small weights are expressed as multiples or fractions of a gram, and larger weights as multiples of a kilogram (1000 grams). This enormously simplifies all calculations which have to be made in chemical analysis. On the other hand, the old English system of weights and measures is still used in practice, and it is therefore necessary to bear in mind the comparative values of the units in the two systems. The accompanying tables give the common English weights and measures, the metrical weights and measures and the comparative values of the units in the two systems. The following remarks may be of service to those who are not familiar with both systems. Having taken the unit of weight as 1 gram, the metric system designates $\frac{1}{10}$, $\frac{1}{100}$, $\frac{1}{1000}$ of this unit by the Latin prefixes deci, centi, and milli. The multiples of grams, that is 10 times, 100 times, 1000 times, are indicated by the Greek prefixes deca, hecto, kilo. In a similar manner the metric units of length and capacity, the meter and liter, are again modified by prefixes to express $\frac{1}{10}$, $\frac{1}{100}$, and $\frac{1}{1000}$, or 10 times, 100 times, 1000 times, etc.

The metric unit of weight, 1 gram, is the weight of one cubic centimeter (c.c.) of water at 4° centigrade. It is as well to remember that there are approximately 28 grams to the ounce, and that a pound is about 454 grams, that is to say, about 50 grams under the half kilogram. The metric unit of length, the meter, is nearly 40 inches ; thus 10 centimeters are approximately equivalent to 4 inches. The measures most commonly used are the millimeter, centimeter, and meter. The measure of capacity is the liter, which is equal to one cubic decimeter or 1000 cubic centimeters. Capacity is usually expressed in cubic centimeters or liters. It is as well to bear in mind that one gallon is equal to about 4½ liters. There is one other point to remember, namely, that the weight of water in grams is obtained directly from its measure by expressing the volume in cubic centimeters seeing that every cubic centimeter of water weighs 1 gram ; thus a liter and a half of water is 1500 c.c., and therefore weighs 1500 grams.

As is well known, the relation between the English weights and measures is not so simple. At the risk of repeating what is already well known, I may state that one gallon of water weighs ten pounds. It is also worth noting that as 70,000 grains of water go to the gallon, grains per gallon are equivalent to parts per 70,000, so that a figure expressed as grains per gallon may be converted into parts per 100,000 by dividing by ·7.

TABLE I.

ENGLISH WEIGHTS AND MEASURES.

Avoirdupois Weight.

ton.	cwts.	qrs.	lb.	oz.	drms.	grains.
1 =	20 =	80 =	2240 =	35840 =	573440	
	1 =	4 =	112 =	1792 =	28672	
		1 =	28 =	448 =	7168	
			1 =	16 =	256 =	7000
				1 =	16 =	437·5
					1 =	27·343

Apothecaries' Weight.

lb.	oz.	drms.	scruples.	grains.
1 =	12 =	96 =	288 =	5760
	1 =	8 =	24 =	480
		1 =	3 =	60
			1 =	20

LONG MEASURE.

mile.	fur.	poles.	fath.	yards.	feet.	ins.
1	8	320	880	1760	5280	63360
	1	40	110	220	660	7920
		1	2¾	5½	16½	198
			1	2	6	72
				1	3	36
					1	12

MEASURES OF CAPACITY (DRY MEASURE).

last.	wey.	quarter.	bushel.	peck.	gall.	pints.
1	2	10	80	320	640	5120
	1	5	40	160	320	2560
		1	8	32	64	512
			1	4	8	64
				1	2	16
					1	8

IMPERIAL MEASURE (LIQUID MEASURE).

gallon.	pints.	fluid oz.	fluid drms.
1	8	160	1280
	1	20	160
		1	8

Note.—One gallon = 10 lb. or 70,000 grains of water; also one cubic foot = 6·2355 gallons, and one gallon = 277·274 cubic inches.

SQUARE MEASURE.

sq. mile.	acre.	rood.	rod or pole.	sq. yd.	sq. ft.	sq. in.
1	640					
	1	4	160	4840	43,560	
		1	40	1210	10,890	
			1	30¼	272¼	
					1	144

CUBIC MEASURE.

cubic yd.	cubic ft.	cubic in.
1	27	46,656
	1	1728

MEASURES FOR TIMBER, ETC.

Load of timber, unhewn or rough .	40 cubic ft.
Load, hewn or squared . . .	50 cubic ft. (reckoned to weigh 20 cwt.).
Stack of wood	108 cubic ft.
Cord of wood	128 cubic ft.
Load of lime	32 bushels.
Load of sand	36 bushels.
Barrel of tar	26½ gallons.

TABLE II.

METRIC WEIGHTS AND MEASURES.

MEASURES OF WEIGHT.

Milligram	=	0·001	gram.
Centigram	=	0·01	,,
Decigram	=	0·1	,,
Gram	=	1·0	,,
Decagram	=	10·0	grams.
Hectogram	=	100·0	,,
Kilogram	=	1000·0	,,

MEASURES OF LENGTH.

Millimeter	=	0·001	meter.
Centimeter	=	0·01	,,
Decimeter	=	0·1	,,
Meter	=	1·0	,,
Decameter	=	10·0	meters.
Hectometer	=	100·0	,,
Kilometer	=	1000·0	,,

MEASURES OF CAPACITY.

Milliliter or cubic centimeter (c.c.)	=	0·001	liter.
Centiliter	=	0·01	,,
Deciliter	=	0·1	,,
Liter	=	1·0	,,
Decaliter	=	10·0	liters.
Hectoliter	=	100·0	,,
Kiloliter	=	1000·0	,,

TABLE III.

ENGLISH AND METRICAL EQUIVALENTS.

DATA FOR CONVERSION OF ENGLISH TO THE METRICAL SYSTEM.

1 ounce (avoirdupois) = 28·35 grams.
1 lb. (avoirdupois) = 453·593 grams.
1 ton = 1016 kilograms.

1 inch = 2·54 centimeters (cm.).
1 foot = ·3048 meter.
1 mile = 1609·3 meters.
1 square foot = ·0929 square meter.

1 pint = 568 cubic centimeters (c.c.).
1 gallon = 4·54 liters.
1 cubic foot = 28·38 liters.

1 pound per square inch = ·0703077 kilogram per square centimeter.
1 pound per square inch = 5·17 centimeters of mercury.
1 grain per gallon = ·0143 gram per liter.
1 pound per gallon = ·998 kilogram per liter.
1 pound per cubic foot = 16·02 kilograms per cubic meter.

1 penny per pound = ·231 franc per kilogram.
£1 per ton = 2·45 francs per 100 kilograms.
£1 per ton = 2·01 marks per 100 kilograms.

To convert—		
Ounces (avoirdupois) to grams	multiply by	28·35
Pounds (avoirdupois) to grams	,, ,,	453·6
Tons to kilograms	,, ,,	1016
Inches to centimeters (cm.)	,, ,,	2·54
Feet to meters	,, ,,	·305
Miles to meters	,, ,,	1609
Square feet to square meters	,, ,,	·093
Pints to cubic centimeters	,, ,,	568
Gallons to liters (square decimeters)	,, ,,	4·54
Cubic feet to liters (square decimeters)	,, ,,	28·4
Pounds per square inch to kilograms per square centimeter	,, ,,	·0703
Pounds per square inch to centimeters of mercury	,, ,,	5·2
Grains per gallon to grams per liter	,, ,,	·014
Pounds per gallon to kilograms per liter	,, ,,	1
Pounds per cubic foot to kilograms per cubic meter	,, ,,	16
Pence per pound to francs per kilogram	,, ,,	·23
£ per ton to francs per 100 kilograms	,, ,,	2·45
£ per ton to marks per 100 kilograms	,, ,,	2

DATA FOR CONVERSION OF THE METRICAL TO THE ENGLISH SYSTEM.

1 gram = 15·4323 grains.
1 kilogram = 2·2046 lb.

1 centimeter = ·3937 inch.
1 meter = 3·281 feet = 39·37 inches.
1 kilometer = ·6214 mile.
1 square meter = 10·764 square feet.

1 cubic centimeter = ·061 cubic inch = ·00176 pint.
1 liter = 61·027 cubic inches = 1·76 pints.
1 cubic meter = 35·32 cubic feet = 220 gallons.
1 kilogram per square centimeter = 14·223 lb. per square inch.

1 centimeter of mercury = ·193 lb. per square inch.
1 gram per liter = 70·12 grains per gallon.
1 kilogram per liter = 10·016 pounds per gallon.
1 kilogram per cubic meter = ·0624 pound per cubic foot.

1 franc per kilogram = 4·32 pence per pound.
1 franc per 100 kilograms = £·4032 per ton.
1 mark per 100 kilograms = £·4974 per ton.

DATA FOR CONVERSION OF ENGLISH TO METRICAL SYSTEM.

To convert—		
Grams to grains	multiply by	15·43
Kilograms to pounds	,, ,,	2·2
Centimeters to inches	,, ,,	·394
Meters to feet	,, ,,	3·28
Kilometers to miles	,, ,,	·62
Square meters to square feet	,, ,,	10·76
Cubic centimeters to cubic inches	,, ,,	·061
Cubic centimeters to pints	,, ,,	·00176
Liters to cubic inches	,, ,,	61·03
Liters to pints	,, ,,	1·76
Cubic meters to cubic feet	,, ,,	35·32
Cubic meters to gallons	,, ,,	220
Kilograms per square centimeter to pounds per square inch	,, ,,	14·2
Centimeters of mercury to pounds per square inch	,, ,,	·19
Grams per liter to grains per gallon	,, ,,	70
Kilograms per liter to pounds per gallon	,, ,,	10
Kilograms per cubic meter to pounds per cubic foot	,, ,,	·0624
Francs per kilogram to pence per pound	,, ,,	4·32
Francs per 100 kilograms to £ per ton	,, ,,	·4
Marks ,, ,, ,, ,,	,, ,,	·5

TABLE IV.

CALCULATION OF AREA AND VOLUME.

Area of a rectangle = length × breadth.
Area of a parallelogram = base × height (measured at right angles to base).
Area of a triangle = base × half the height.
Circumference of a circle = $2\pi r$.
Area of a circle = πr^2.
$\pi = 3{\cdot}1416$.
r = radius of circle.
Area of an oval or ellipse = $\frac{1}{2}$ long diameter × $\frac{1}{2}$ short diameter × π.
Volume of a prismatic or cylindrical body = area of base × height.

$$\text{Volume of a pyramid or cone} = \frac{\text{area of base} \times \text{height}}{3}.$$

$$\text{Volume of a sphere} = \frac{4}{3}\pi r^3.$$

$$\text{Contents of a barrel (approx.)} = \frac{\pi l}{3} \times (2R^2 + r^2),$$

where l = height or length of barrel,
R = half the diameter at the middle,
r = half the diameter at either end,
all measurements being made on the inside.

CHAPTER II.

METHODS OF CHEMICAL ANALYSIS.

Chemical testing is conveniently divisible into qualitative and quantitative analysis.

The former concerns itself merely with detecting the presence of substances in admixture with others or with identifying a given substance. On the other hand, it is the object of quantitative analysis, as its name implies, to determine the amount of a substance present.

Thus we may ascertain that a particular rag-paper contains rosin so that we are justified in concluding that it is engine-sized. This is merely a qualitative test ; it becomes quantitative when we proceed to determine the amount of rosin contained in a given weight of paper.

A convenient well-lighted room should be set apart for carrying out the necessary chemical, microscopical, and other tests. It should be provided with a firm wooded bench with shelves above and drawers and cupboards underneath. The whole may be made of plain deal, although the top is preferably constructed of some harder wood such as teak, and should not be less than one inch thick. An ample water supply and a sink are also necessary. The latter should be let into the middle of the bench and not in the corner of the room where it is difficult for more than one person to use at a time. A good light too is as necessary for the sink as for the other parts of the bench, as you want to see exactly what you are doing when, for instance, you are washing some bleached fibre or even cleaning apparatus. The water-supply pipe should have at least two branches each provided with a separate tap so that when one is connected with a condenser, for instance, the other is available for drawing water or other purposes. Close to the sink a slanting rack may be arranged for draining apparatus that has been washed. Heating is most conveniently effected with gas. Branches of the gas main should lead to different parts of the bench so that one or more Bunsen burners may be used at the same time. When gas is not available spirit and petroleum lamps are used, the latter specially constructed to yield a colourless flame and may be obtained from the usual chemical dealers.

Weighing.—Perhaps the most necessary apparatus is the balance and weights. Two such should be provided. A rough balance or pair of scales to carry at least a kilogram and sensitive to $\frac{1}{10}$ gram, and a delicate balance to carry 100 grams and sensitive to $\frac{1}{10}$ to 1 milligram. Each balance is provided with its own set of weights.

As the proper method of handling a balance is not often rightly understood, I give here a list of rules explaining exactly what to do and what not to do.

1. Place the substance to be weighed on the left-hand pan and the weights on the right.
2. Never put a chemical substance directly on the scale pan, but on a watch glass or other suitable dish or even sheet of paper which has previously been weighed (tared) or counterpoised.
3. Never put a hot crucible on the scale pan, but wait until it is quite cold.
4. When starting to weigh move slowly the milled head that sets the beam free to swing, keeping the eye on the pointer.
5. Never put anything on or take anything off either pan without arresting the beam and stopping the swing.
6. Start weighing, using if anything too heavy a weight, and try the lighter weights regularly in succession.
7. When the pointer swings the same number of divisions in both directions the correct weight has been found. Note the weight immediately in a notebook before removing the weights, then check the weight that has been written down by removing the weights one by one.

These directions apply generally to both balances, but especially to the fine balance. If roughly handled a good balance soon begins to lose accuracy. The weights for the fine balance may be conveniently kept on a piece of card marked out in divisions on the floor of the balance case, as shown in figure 1; a glance at the card is sufficient to show what weights have been taken off and put on the pan as the numbers are thereby left uncovered.

50	20	10	10	5	2	1	1
·5	·2	·1	·1	·05	·02	·01	·01

FIG. 1.—Card for Weights in Balance Case.

Drying.—Some substances are "hygroscopic"—that is to say, they absorb moisture from the air; and, therefore, increase in weight while being weighed unless precautions are taken. They should be weighed in small light glass stoppered bottles (fig. 2), known as weighing bottles. This precaution must be taken with all paper-making fibres after drying, including paper itself, as in this condition they rapidly take up moisture from the atmosphere and increase in weight. This does not, however, apply where the fibres are weighed "air-dry," that is to say, holding the small amount of moisture they normally contain.

FIG. 2.

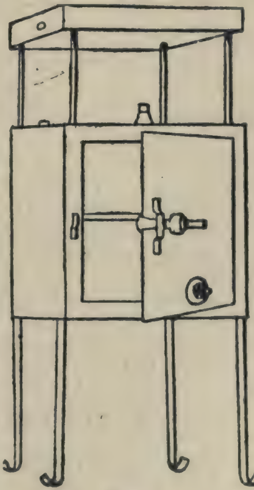


FIG. 3.

For drying small quantities of fibre or other substances it is necessary to provide an air or steam bath.

The former consists merely of a copper box with hinged door provided with ventilating holes and heated with burner underneath (fig. 3). For most purposes the temperature is regulated so that it stands between 100° and 110° C., which is quite high enough to drive off all moisture. The steam bath is constructed on the same lines as the air bath, but the walls are double, so that they form a jacket to contain water which is kept just boiling by a burner underneath. The temperature in such a bath cannot, of course, rise above 100° C., and is usually a degree or so lower. Substances to be dried should be spread out in a thin layer. Fibrous material is conveniently held in paper trays, merely rectangular pieces of smooth glazed paper with the edges turned up. Chemicals are more conveniently dried on watch glasses or in open dishes.

Evaporation.—It is often necessary to evaporate liquids to concentrate them and get rid of a part or the whole of the water. An evaporating dish or basin (fig. 4) of porcelain is the most suitable vessel to use, but glass beakers are also serviceable in some cases.

The dish is either heated directly with a flame by supporting it on wire gauze on a tripod, or with steam on a water bath. This is nothing but a metal pan (a saucepan does very well), with a cover made of a series of flat rings of different apertures to take different-sized dishes. A water bath must always be used in the last stages of evaporation, if it is desired to take the liquid down to dryness. Porcelain dishes should always be used for boiling alkaline liquids, in preference to glass, as the latter are acted on and get broken sooner or later. For small quantities of liquid, platinum dishes are very convenient and allow of rapid working, especially if the solid residue is to be dried and weighed, and then ignited. They are of course very expensive, but as they do not break and only wear away very slowly, with judicious handling, they are economical when saving of time and accuracy are taken into consideration.

FIG. 4.

Ignition.—Here, again, platinum dishes and crucibles are extremely serviceable; they can be heated more quickly and completely, cool more quickly and take up less moisture when being weighed than porcelain. Paper and fibrous materials are burnt to determine the percentage of ash, *i.e.* mineral matter. Platinum crucibles should be supported on clay triangles and placed in a slanting position, the more so the better, provided that there is no danger of the material falling out. This allows freer access of air and any carbonised residue is more rapidly burnt off. These same considerations apply to the ignition of precipitates, such as sulphate of barium.

Precipitation and Filtration.—Precipitation is resorted to in the analysis of such chemicals as alum, in which one or other constituent is brought into an insoluble condition. Thus aluminium is precipitated as hydroxide with ammonia solution. The insoluble part or precipitate is collected on a filter paper, thoroughly washed by the addition of successive small quantities of water till all soluble substances are washed out. The moist precipitate is dried and ignited to burn off the filter paper and the dry precipitate weighed.

The weight of the precipitate, in this case, aluminium oxide, gives the weight of alumina in the alum originally taken.

One or two precautions should be taken. When pouring liquids from one vessel to another, always pour down the side of a glass rod. This will avoid loss from splashing. The filter paper should be carefully fitted in the funnel, and then moistened with distilled water. After this has been properly done, the paper will adhere evenly to the glass all the way round, and on pouring in the liquid it will filter more quickly than with a badly fitting paper. The filter should not be filled more than two-thirds with the liquid, and must on no account be filled to the brim. It is usually more effective when washing a precipitate to allow one lot of wash water to drain away completely before adding the next. Distilled water should be used for washing, and may be directed on to the precipitate by a jet from a wash bottle, but care must be taken not to blow too violently, otherwise some of the precipitate may splash out.

The precipitates mostly dealt with in paper analyses need not be dried before weighing when igniting in a platinum crucible. The precipitate is put into the crucible while still moist, and a full flame set underneath; there is usually a little sizzling but no splashing, and much time is saved without loss of accuracy. The

Bunsen burner should have the air-holes open so that the flame is colourless, and any deposit of soot on the platinum should be avoided. The platinum crucible containing the precipitate may be rapidly cooled before weighing by placing it on a glazed porcelain tile.

Notes and Calculations.—All notes should be entered in a notebook while the work is in progress, and directly a weighing is finished the weights should be entered up. This is best done as follows:—

Weight of crucible + ppte. = 35·776
Weight of crucible = 34·652
∴ weight of ignited ppte. ($BaSO_4$) = 1·124

"Ppte." is a convenient abbreviation for the word "precipitate".

Having obtained the weight of the precipitate the next step is to calculate the weight of the substance or ingredient it is desired to determine. This will be much simplified by making use of the table of factors, Table VII., given on page 22, and a slide rule may be used to facilitate the final calculation. As an example, the determination of the weight of sulphuric anhydride (SO_3) in a sample of alum may be taken:—

One gram of a fair sample of the powdered alum having been weighed out, it is dissolved in water, and the sulphuric acid precipitated as barium sulphate. After filtering off the precipitate, washing and igniting it, we will assume that the above figures were obtained. Our data as they stand at present are that 1 gram of alum has yielded 1·124 grams of barium sulphate. If now we turn up sulphuric anhydride in the table of factors under the "sought" column, taking the barium sulphate under the "found" column, we find the factor ·3429 given, hence 1·124 × ·3429 = ·3854, that is to say, 1 gram of alum contains ·385 gram of sulphuric anhydride; in other words, the sample of alum in question contains 38·5 per cent (SO_3).

Volumetric Analysis. — Where possible the chemist adopts the method of volumetric analysis in preference to the gravimetric, especially where a large number of the same kind of analyses have to be carried out. The volumetric method is more rapid and equally accurate, as measuring by volume is quicker than weighing.

A measuring flask (fig. 5) is usually employed for obtaining a known volume of a liquid. It consists merely of a flask with a narrow neck on which a mark is engraved. The flasks are made in various sizes, so as to hold 1000, 500, 250, 200 and 100 c.c. when filled with water at 60° F. (or 15° C.) to the mark on the neck. These flasks are commonly employed in making up a solution of known strength, or diluting solutions to known volumes. Where a high degree of accuracy is unnecessary, measuring flasks may be replaced by measuring cylinders (fig. 6). These consist of tall graduated cylinders of thick glass.

Both measuring cylinders and measuring flasks are generally graduated to hold or contain the volume marked upon them. Sometimes, however, they are required to deliver a given volume, and as a small quantity of liquid remains behind in the flask even after well draining, the mark on the neck requires to be placed a little higher when the flask is used for delivering. Some flasks are provided

FIG. 5.

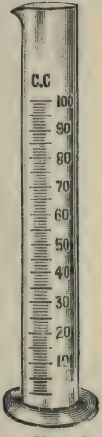


FIG. 6.

FIG. 7.

FIG. 8.

with two marks, the lower one being for measuring and the upper for delivering.

For delivering small quantities of liquid a pipette is frequently used. It consists of a tube, either with a single mark on the upper and narrow part of the tube, the central portion being blown into the form of a bulb (fig. 7), or of a straight tube of even bore graduated throughout the greater part of its length (fig. 8). The first form is suitable for delivering fixed volumes and the latter for delivering varying quantities. The pipette should be first washed out with a little of the liquid to be delivered. The point of the pipette is placed in the liquid which is sucked up to a point just above the mark, by applying the lips to the upper end;[1] it is then rapidly closed with the finger; then, on gradually relaxing the pressure of the finger, the level of the liquid is allowed to sink to the mark. The measured quantity of liquid now remaining in the pipette is allowed to run out into the vessel as may be required. The second form of graduated pipette is not much used, except for delivering very small quantities, such as 10 c.c., or less. For most purposes it is replaced by the burette (fig. 9), which consists of a long graduated tube of even bore, provided at the bottom with a stopcock. The burette is first washed out with the liquid to be used and then filled almost to the brim; the tap at the bottom is then opened and part allowed to run out till the level sinks to the first graduation. It can now be used for delivering the requisite quantity of liquid by merely manipulating the tap, but care must be taken to see that no air bubbles are

FIG. 9.

---

[1] Pipettes should not be used for strong acids, alkalies or other liquids, which might do serious harm if sucked up into the mouth. Fatal accidents have happened in this manner.

entangled and that the bottom of the tube to the very point of the jet is full of liquid. Burettes are usually made to deliver 50 c.c. and graduated in tenths of a c.c., but smaller sizes are sometimes handy.

The reader is referred to books devoted to chemical analysis (volumetric analysis) for further details,[1] but the method of using the different apparatus will be better understood when we come to the actual description of analytical processes.

The principle on which volumetric analysis is based may be summed up as follows :—

Standard solutions are prepared containing known quantities of the reagent, and sufficient of the standard solution is added to complete the reaction and the volume noted. Knowing the strength of the standard solution, it is easy to calculate the amount of reagent which has been used for completing the reaction.

Standard solutions are prepared either of so-called normal strength, or more dilute, such as $\frac{1}{10}$ (decinormal) or $\frac{1}{100}$ (centinormal). These are made by diluting the normal solutions to 10 or 100 times their original volume, and are shortly represented by the symbols : $N, \frac{N}{10}$ or $\frac{N}{100}$. Thus, supposing we have a normal solution from which we require to prepare a decinormal solution, 50 c.c. of the former are delivered by means of a pipette into a 500 c.c. flask which is then made up to the mark with distilled water and the contents thoroughly mixed.

A normal solution is prepared by dissolving an "equivalent" weight in grams in 1 liter of distilled water. "Equivalent" weights are either identical with molecular weights or simple fractions of these, usually one-half (see Table VIII.). Thus the equivalent weight of hydrochloric acid is equal to its molecular weight, that is to say, it is the sum of the atomic weights of its constituent elements ; thus, $H = 1, Cl = 35{\cdot}5 \therefore 1 + 35{\cdot}5 = 36{\cdot}5$, the molecular weight and, in this instance, also the equivalent weight. A normal solution of hydrochloric acid, therefore, contains 36·5 grams of pure dry hydrochloric acid dissolved in 1 liter of water.

On the other hand, the equivalent weight of sodium

---

[1] *Quantitative Analysis*, by Clowes and Coleman, may be recommended.

carbonate (Na_2CO_3) is equal to half its molecular weight, thus:

$$\frac{46 + 12 + 48}{2} = 53.$$

A normal solution of sodium carbonate may be prepared by dissolving 53 grams of the pure dry substance in 1 liter of water; on the other hand, hydrochloric acid is a gas, and cannot be conveniently weighed, and the solution of the gas which goes under the name of hydrochloric acid is of varying strength. Other means must, therefore, be found for preparing a normal solution of this substance.

In virtue of the fact that all normal solutions contain the equivalent weights in grams dissolved in the same quantity (1 liter) of water, the normal solutions themselves are always equivalent to one another; that is to say, if we take the case of normal solutions of acids and alkalies, equal volumes of these will always exactly neutralise one another. This principle of equivalency is the basis of volumetric analysis, and should never be lost sight of.

The same considerations of course apply to decinormal and centinormal solutions, as they are diluted proportionately. Any particular number, say, 15 c.c. of $\frac{N}{10}Na_2CO_3$, will always require 15 c.c. of $\frac{N}{10}(HCl)$ or $\frac{N}{10}H_2SO_4$ or any other decinormal acid to neutralise them. If then a normal Na_2CO_3 solution has been prepared by weighing out the requisite quantity of dry sodium carbonate and dissolving in a liter of water, normal HCl solution is easily obtained by diluting a quantity of the strong solution of this acid until it is exactly neutralised by an equal volume of normal Na_2CO_3 solution. Normal sulphuric acid is prepared in a similar manner, and having obtained normal acids the normal caustic alkalies may be prepared by dissolving approximately the correct quantity in water and then strengthening or diluting, as may be required, until the solution is neutralised by the same volume of normal acid. As Na_2CO_3 is the basis for the standardisation of the other acids and alkalies, care must be taken to see that this solution is made up to the correct strength. Pure anhydrous sodium carbonate of sufficient purity may now be bought. It should, however, be gently ignited in a platinum dish to ensure its freedom from moisture before weighing; or it may be prepared by gently igniting to a dull redness for twenty minutes the bicarbonate of soda which is readily obtained pure. To make certain that the whole of the bicarbonate has been converted into normal carbonate, the dish should be allowed to cool in a desiccator and weighed, and the process of heating repeated until no further loss of weight ensues. The platinum dish is first weighed, and if bicarbonate is used 9 grams should be roughly weighed out into it. If pure normal carbonate is used 5½ to 6 grams will be required. After igniting to a constant weight small portions are removed from the dish until exactly 5·306 grams remain which are then dissolved in water and made up to 100 c.c., if a normal solution be required, or 1000 c.c. if a decinormal solution.

For the preparation of normal sulphuric acid, about 30 c.c. of pure concentrated acid are added gradually to 200 or 300 c.c. of water in a flask. When the mixture is cold, it is diluted and made up to 1000 c.c. For the preparation of normal hydrochloric acid about 150 c.c. of the strong acid is diluted to 1 liter. Having thus prepared approximately normal sulphuric and hydrochloric, the strength is accurately determined by taking 20 c.c. with a pipette and titrating with normal sodium carbonate solution. For this purpose the latter is placed in a burette and added in small quantities at a time to the acid contained in a beaker, flask or dish, and previously diluted with a little water. The point at which the whole of the acid is neutralised by the carbonate of soda is determined by the addition of two drops of a solution of methyl orange. The natural yellow colour of methyl orange is turned intensely red by an acid, and then yellow again when the acid is neutralised with an alkali. Sufficient carbonate of soda solution is added from a burette to destroy every trace of red colour and *just* restore the colour of the solution to a pure yellow. At this point the acid is exactly neutralised by the carbonate of soda, and the volume that has been required is read off on the burette. The change of colour is easily followed if a couple of drops of the methyl orange be added to a smaller flask or other vessel containing an equal volume of water only. This liquid will be pure yellow, and will show what the final colour of the neutralised acid should be.

If the strength of the acid thus determined should not be correct, a simple calculation is all that is required to determine how much more water or how much more acid is required to render the solution exactly normal. After the addition has been made and the liquid well mixed, another 20 c.c. should be titrated with normal sodium carbonate, and if still too strong or too weak, further correction must be made until exactly 20 c.c. of the alkali are required for neutralisation.

Besides methyl orange other indicators may be used. In general, methyl orange should be used for titrating strong acids, bases and carbonates, but for the titration of weak acids another indicator, phenol phthalein, is required. This body is a white substance, which must be dissolved in weak alcohol. A drop or two of the solution is added to the liquid, which remains colourless in the presence of acids, but is turned intense red by traces of alkalies. A standard solution of *caustic* alkali is necessary for titrations of this class.

Litmus is a convenient indicator to use in some cases. As is well known, it is turned red by acids and blue by alkalies. Weak acids like carbonic acid have some action on it so that the solution must be heated to boiling to drive off carbon dioxide gas, if this indicator is used for titrating alkaline carbonates. Litmus paper is also handy in some cases, preferably that prepared from sized paper.

Volumetric analysis is not confined to the titration of acids and alkalies; the method is also adapted for the analysis of bleach, antichlor and other chemicals, to which reference will be made in the proper place.

TABLE V.

ATOMIC WEIGHTS OF THE COMMONER ELEMENTS.

Element.	Symbol.	Exact Atomic Weight.	Approximate Atomic Weight.
Aluminium .	Al	27·1	27
Antimony . .	Sb	120·2	120
Arsenic . . .	As	74·96	75
Barium . . .	Ba	137·37	137
Bismuth . . .	Bi	208·0	208
Boron	B	11·0	11

TABLE V. (*continued*).

Element.	Symbol.	Exact Atomic Weight.	Approximate Atomic Weight.
Bromine	Br	79·92	80
Cadmium	Cd	112·40	112
Calcium	Ca	40·07	40
Carbon	C	12·005	12
Chlorine	Cl	35·46	35·5
Chromium	Cr	52·0	52
Cobalt	Co	58·97	59
Copper	Cu	63·57	64
Fluorine	F	19·0	19
Gold	Au	197·2	197
Hydrogen	H	1·008	1
Iodine	I	126·92	127
Iron	Fe	55·84	56
Lead	Pb	207·20	207
Magnesium	Mg	24·32	24
Manganese	Mn	54·93	55
Mercury	Hg	200·6	201
Molybdenum	Mo	96·0	96
Nickel	Ni	58·68	59
Nitrogen	N	14·01	14
Oxygen	O	16·00	16
Phosphorus	P	31·04	31
Platinum	Pt	195·2	195
Potassium	K	39·10	39
Silicon	Si	28·3	28
Silver	Ag	107·88	108
Sodium	Na	23·00	23
Strontium	Sr	87·63	88
Sulphur	S	32·06	32
Thorium	Th	232·4	233
Tin	Sn	118·7	119
Titanium	Ti	48·1	48
Tungsten	W	184·0	184
Zinc	Zn	65·37	65

Note.—This list is compiled from the international atomic weights, 1917, omitting the rarer elements. For most purposes the approximate atomic weights given in the second column are sufficiently accurate.

TABLE VI.

FORMULÆ AND MOLECULAR WEIGHTS OF THE MORE IMPORTANT CHEMICAL SUBSTANCES USED FOR ANALYSIS AND IN THE PAPER INDUSTRY.

Name of Substance.	Formula.	Mol. Weight.
Aluminium oxide (alumina)	Al_2O_3	102
[1] Aluminium sulphate	$Al_2(SO_4)_3$	342
Ammonia	NH_3	17
,, alum	$Al_2(SO_4)_3 . (NH_4)_2SO_4 . 24H_2O$	907
Barium carbonate	$BaCO_3$	197
,, hydroxide	$Ba(OH)_2$	171
,, oxide	BaO	153
,, sulphate	$BaSO_4$	233
Borax (sodium borate)	$Na_2B_4O_7 . 10H_2O$	382
Boric (or boracic) acid	H_3BO_3	62
Calcium carbonate	$CaCO_3$	100
,, chloride	$CaCl_2$	111
,, hydroxide (slaked lime)	$Ca(OH)_2$	74
,, oxide (quicklime)	CaO	56
,, sulphate	$CaSO_4$	136
Carbon dioxide (carbonic anhydride)	CO_2	44
Copper oxide	CuO	80
,, sulphate	$CuSO_4 . 5H_2O$	250
Ferric and ferrous. (See Iron.)		
Hydrochloric (muriatic) acid	HCl	36·5
Iron chloride (ferric chloride)	$FeCl_3$	162
,, ,, (ferrous chloride)	$FeCl_2$	127
,, oxide (ferric oxide)	Fe_2O_3	160
,, pyrites	FeS_2 (mostly)	120
,, sulphate (ferric sulphate)	$Fe_2(SO_4)_3$	400
,, ,, (ferrous sulphate) crystals	$FeSO_4 . 7H_2O$	278
Lead acetate	$PbC_4H_6O_4$	325
,, chromate	$PbCrO_4$	323
,, sulphate	PbS_4O	303
Magnesium carbonate	$MgCO_3$	84
,, oxide	MgO	40
,, sulphate	$MgSO_4 . 7H_2O$	246·5
,, pyrophosphate	$Mg_2P_2O_7$	223
Nitric acid	HNO_3	63
Potash alum	$Al_2(SO_4)_3 . K_2SO_4 . 24H_2O$	949
Potassium carbonate	K_2CO_3	138
,, chloride	KCl	75
,, ferricyanide	$K_3Fe(CN)_6$	330
,, ferrocyanide	$K_4Fe(CN)_6 . 3H_2O$	423
,, hydroxide	KOH	56

---

[1] Incorrectly but often termed "alum".

TABLE VI. *(continued)*.

Name of Substance.	Formula.	Mol. Weight.
Potassium iodide	KI	166
,, nitrate (nitre)	KNO_3	101
,, oxide	K_2O	94
,, permanganate	$KMnO_4$	158
,, sulphate	K_2SO_4	174
,, sulphocyanide or thiocyanate	$KCNS$	97
Silica	SiO_2	60
Silver chloride	$AgCl$	143
,, nitrate	$AgNO_3$	170
Sodium bicarbonate	$NaHCO_3$	84
,, bisulphite	$NaHSO_3$	104
,, carbonate (soda ash)	Na_2CO_3	106
,, ,, (soda crystals)	$Na_2CO_3 . 10H_2O$	286
,, chloride (common salt)	$NaCl$	58·5
,, hydroxide (caustic soda)	$NaOH$	40
,, oxide	Na_2O	62
,, sulphate (salt cake)	Na_2SO_4	142
,, ,, (crystals)	$Na_2SO_4 . 10H_2O$	322
,, sulphite	Na_2SO_3	126
,, ,, (hydrate)	$Na_2SO_3 . 7H_2O$	252
,, thiosulphate (hyposulphite)	$Na_2S_2O_3 . 5H_2O$	248
Sulphur dioxide	SO_2	64
,, trioxide	SO_3	80
Sulphuric acid	H_2SO_4	98
Sulphuretted hydrogen	H_2S	34
Tin chloride (stannous chloride)	$SnCl_2 . 2H_2O$	226
Zinc chloride	$ZnCl$	136
,, sulphate	$ZnSO_4 . 7H_2O$	287

TABLE VII.

FACTORS FOR ANALYSIS.

These facilitate the calculation of results from the weights obtained in gravimetric analysis or from the volumes of standard solutions required in volumetric analysis.

Method of Calculation.—To find the weight of substance in the first column multiply the weight in grams of the substance found in the second column by the factor in the third column.

TABLE VII. (*continued*).

Sought.	Found.	Factor.
Al	Al_2O_3	0·5303
Ba	$BaSO_4$	0·5885
BaO	$BaSO_4$	0·6571
Ca	CaO	0·7143
Ca	$CaCO_3$	0·4000
CaO	$CaCO_3$	0·5600
Cl	AgCl	0·2472
Cl	HCl	0·9724
Cu	CaO	0·7982
Fe	Fe_2O_3	0·7000
Fe	FeO	0·7775
Fe_2O_3	Fe	1·4292
FeO	Fe	1·2861
HCl	AgCl	0·2542
HCl	Cl	1·0282
H_2SO_4	$BaSO_4$	0·4200
Mg	$Mg_2P_2O_7$	0·2188
MgO	$Mg_2P_2O_7$	0·3624
Si	SiO_2	0·4670
S	$BaSO_4$	0·1373
SO_2	$BaSO_4$	0·2744
SO_3	$BaSO_4$	0·3429
SO_4	$BaSO_4$	0·4115

Method of Calculation.—To find the weight of substance in the first column when titrating with the standard solution in the second column, multiply by the coefficient in the third column.

Acidimetry or Titration of Acids.

Sought.	Standard Solution.	Coefficient.
H_2SO_4	Normal alkali	0·049
SO_4	,, ,,	0·048
SO_3	,, ,,	0·040
HCl	,, ,,	0·0365
Cl	,, ,,	0·0355
Rosin (abietic and other acids)	,, ,,	0·346
$Ba(OH)_2$	Normal acid	0·0855
$BaCO_3$	,, ,,	0·0985
$Ca(OH)_2$	,, ,,	0·037
CaO	,, ,,	0·028
$CaCO_3$	,, ,,	0·05
KOH	,, ,,	0·056
K_2O	,, ,,	0·047
K_2CO_3	,, ,,	0·069
MgO	,, ,,	0·02
NaOH	,, ,,	0·040
Na_2O	,, ,,	0·031
Na_2CO_3	,, ,,	0·053

TABLE VII. (*continued*).

Sought.	Standard Solution.	Coefficient.
NH_3	Normal acid	·017
NH_4OH	,, ,,	·035
NH_3 (as protein in Kjeldahl's estimation)	,, ,,	·875
Cl	$\frac{N}{10}$ silver nitrate	0·00355
HCl	,, ,,	0·00365
As_2O_3	$\frac{N}{10}$ iodine	0·00495
H_2SO_3	,,	0·0041
SO_2	,,	0·0032
Na_2SO_3	,,	0·0063
$Na_2S_2O_3 . 5H_2O$	,,	0·0248
Cl	$\frac{N}{10}$ thiosulphate	0·00355
I	,,	0·0127
Cl	$\frac{N}{10}$ arsenious acid	0·00355
Ca	$\frac{N}{10}$ permanganate	0·002
CaO	,,	0·0028
$CaCO_3$	,,	0·005
Fe	,,	0·0056
FeO	,,	0·0072
Fe_2O_3	,,	0·008
CaO	$\frac{N}{10}$ oxalic acid	0·0028

TABLE VIII.

WEIGHTS OF SUBSTANCES IN GRAMS WHICH, DISSOLVED IN A LITER OF WATER, YIELD DECINORMAL SOLUTIONS.

Sulphuric acid	H_2SO_4	4·9
Hydrochloric acid	HCl	3·65
Sodium hydroxide	NaOH	4·0
*Sodium carbonate	Na_2CO_3	5·3
Ammonium hydroxide	NH_4OH	3·5
*Silver nitrate	$AgNO_3$	17·0
*Arsenious oxide	As_2O_3	4·95
*Iodine	I	12·7
*Sodium thiosulphate	$Na_2S_2O_3 . 5H_2O$	2·48
*Potassium permanganate	$KMnO_4$	3·16
*Oxalic acid	$C_2H_2O_4 . 2H_2O$	6·3

For normal solutions ten times these quantities will be contained in a liter of the solution. Normal solutions are seldom required except in the case of acids and alkalies. For most purposes decinormal solutions are used. Only those substances marked with an asterisk can be prepared by weighing out, dissolving in water, and making up to a known volume. Arsenious oxide requires the addition of sodium carbonate to bring it into solution, and iodine the addition of potassium iodide.

TABLE IX.

FORMULÆ AND SOLUBILITIES OF SOME COMMON SUBSTANCES IN COLD AND BOILING WATER.

Substance.	Formula.	Parts of Substance Soluble in 100 parts Water.	
		Cold 15° C.	Boiling 100° C.
Aluminium sulphate	$Al_2(SO_4)_3$	34	89
Ammonia alum	$Al_2(SO_4)_3 . (NH_4)_2SO_4 . 24H_2O$	13	422
Potash alum	$Al_2(SO_4)_3 . K_2SO_4 . 24H_2O$	12	357
Barium chloride . . .	$BaCl_2$	34	58
,, hydroxide . . .	$Ba(OH)_2$	3·2	100 (at 80° C.)
,, nitrate	$Ba(NO_3)_2$	8	32
Borax (sodium borate) . .	$Na_4B_2O_7 . 10H_2O$	6	201
Calcium carbonate . . .	$CaCO_3$	·003	Less soluble than in cold water
Water saturated with carbonic acid dissolves		·1	—
Calcium chloride	$CaCl_2$	66	157
,, hydroxide (slaked lime)	$Ca(OH)_2$	·15	·08
,, nitrate	$Ca(NO_3)_2$	100	350
,, oxide (quicklime) . .	CaO	·13	·06
,, sulphate (gypsum) .	$CaSO_4 . 2H_2O$	·26	·21
,, ,, (anhydrous) .	$CaSO_4$	·20	·16
,, sulphite	$CaSO_3$	·13	—
Copper sulphate	$CuSO_4 . 5H_2O$	40	203
Ferrous sulphate (sulphate of iron or copperas)	$FeSO_4 . 7H_2O$	70	33
Lead acetate (sugar of lead) .	$Pb(C_2H_3O_2)_2 3H_2O$	66	200
,, chloride	$PbCl_2$	·74	More soluble than in cold wate

TABLE IX. (*continued*).

Substance.	Formula.	Parts of Substance Soluble in 100 parts Water.	
		Cold 15° C.	Boiling 100° C.
Lead chloride dissolves more readily in water containing hydrochloric acid			
Lead nitrate	$Pb(NO_3)_2$	50	140
,, sulphate	$PbSO_4$	·003	—
Lime. (See calcium oxide.)			
Magnesium carbonate	$MgCO_3$	·003	—
Water saturated with carbonic acid dissolves		·13	—
Magnesium chloride	$MgCl_2 . 6H_2O$	100-200	More soluble than in cold water
,, oxide	MgO	·002	—
Potassium bichromate	$K_2Cr_2O_7$	9	100
,, chromate	K_2CrO_4	60	80
,, ferrocyanide	$K_4Fe(CN)_6 . 3H_2O$	25	95
Sodium acetate	$NaC_2H_3O_2 . 3H_2O$	33	—
,, carbonate (soda ash)	Na_2CO_3	12	45
,, ,, (soda crystals)	$Na_2CO_3 . 10H_2O$	93	540
,, bichromate	$Na_2Cr_2O_7$	109	163
,, hydroxide	$NaOH$	Very soluble, especially in hot water	
,, thiosulphate (hyposulphite)	$Na_2S_2O_3 . 5H_2O$	50	200
,, sulphite	Na_2SO_3	20	—
Tin chloride (stannous chloride)	$SnCl_2$ and $SnCl_2 . 2H_2O$	100-200	—
A large proportion of water decomposes stannous chloride, but it is soluble without decomposition in HCl			
Zinc sulphate	$ZnSO_4$	50	95
	and		
	$ZnSO_4 . 7H_2O$	150	654

Remarks.—The solubility of substances often differs according to the method employed in preparing them. Many of the less soluble substances are only dissolved to the maximum extent on long standing with water.

Of the substances given above calcium chloride, sodium bichromate, and sodium hydroxide (caustic soda) are hygroscopic, *i.e.* absorb moisture from the air, and must be kept in well-closed receptacles or the moisture they absorb will dissolve them as they are all soluble in very small quantities of water.

Specific Gravity.—The specific gravity of solid or liquid substances is the ratio of the weight of any given volume of the substance to an equal volume of water. The term has not exactly the same meaning as density, which is the weight of the unit volume of a substance. As, however, the weight of a unit volume of water equals 1, it follows that the figures representing the value for specific gravity and density are identical, and hence for practical purposes the terms are interchangeable. The density of solid substances is sometimes determined with a view to checking their purity; but we are more often concerned with the determination of the density of liquids.

If we dissolve common salt in water, the density of the liquid will increase with the amount of salt in solution. The increase will not be directly proportional to the strength of the salt solution, but will, nevertheless, bear a certain relation to it, and if the density of salt solutions of different concentrations be determined once for all and tabulated, it will only be necessary after determination of the density to refer to this table to find the percentage of salt dissolved in any particular solution. Such tables as these will be found on pages 69, 73, etc., and are very handy for checking the strength of solutions of caustic soda, acids and other liquids. The approximate density of a liquid is easily determined by means of a hydrometer.

Hydrometers.—These instruments are almost exclusively used in practice for determination of density or specific gravity of fluids. For more accurate work a specific gravity bottle, Sprengel's tube or other device is chosen, but for most purposes the hydrometer gives sufficiently accurate results, provided the graduations are correctly marked in the first instance. It is as well to check the readings obtained with a new hydrometer either by one or two parallel readings with one that is known to be accurate, or by means of a few determinations made with a specific gravity bottle. Some of the cheaper hydrometers are very badly constructed, and give readings with very appreciable errors.

Hydrometers may be graduated on several different systems, and it is unfortunate that no one system has found general acceptance. As a rule they are not graduated to read the sp. gr. straight away but according to some arbitrary scale from which the actual sp. gr. may either be calculated or obtained by reference to a table. We are fortunate in this country in possessing the Twaddell system, which is perhaps the most rational of any devised. For ordinary purposes it has found almost universal acceptance in Great Britain, while on the Continent great confusion prevails owing to the different systems adopted in different places at different times; the Baumé scale is that now most generally found. In America a form of Baumé is employed differing from that used on the Continent. To calculate degrees Twaddell from the actual specific gravity multiply by 1000, discard the first figure 1 and divide by 5. Thus a sp. gr. of 1·025 multiplied by 1000 gives 1025, and on discarding the figure 1 there remains 25. This divided by 5 gives the result in degrees Twaddell, namely, 5°. Similarly 30° Tw. = 1·150 or 100° Tw. = 1·500, etc.

This relation may be expressed in the form of an equation, thus :—

$$\text{Sp. gr.} = (\text{Tw.} \times 5) + 1000$$

$$\text{and} \qquad \text{Tw.} = \frac{\text{Sp. gr.} \quad - 1000}{5},$$

the sp. gr. of water being taken as 1000 and Tw. representing degrees Twaddell.

Degrees on the (Continental or rational) Baumé scale may be reduced to sp. gr. by the following equations, B. representing degrees Baumé :—

$$\text{Sp. gr.} = \frac{144{\cdot}3}{144{\cdot}3 - \text{B.}}$$

$$\text{B.} = 144{\cdot}3 - \frac{144{\cdot}3}{\text{sp. gr.}}.$$

The American Baumé degrees are related to the sp. gr. by the following formulæ :—

$$\text{Sp. gr.} = 145 - \frac{145}{\text{B.}}.$$

$$\text{B.} = \frac{145}{145 - \text{sp. gr.}}.$$

There is also a Dutch formula,

$$\text{Sp. gr.} = \frac{144}{144 - \text{B.}}$$

closely on the lines of the above Continental scale.

On pages 30-33 will be found Tables XI. and XII. giving in parallel columns the sp. gr. in terms of the Continental Baumé and Twaddell; and also the sp. gr. corresponding to the Continental and American Baumé degrees.

A word of caution is necessary in the use of hydrometers. The principle on which they are constructed is such that the results hold good only when the liquids are approximately free from impurities. Any large amount of impurity upsets the calculation. As will be readily understood the impurities affect the density of a solution just in the same way as the substance itself. To take an example. In many mills a hydrometer is used for taking the strength of the bleach liquor. If the bleach is of poor quality, very misleading results can be obtained, as calcium chloride, a body remaining over when bleach decomposes, raises the gravity of the bleach liquor just as bleach itself does. The hydrometer will serve as a useful check for rough purposes, but the only reliable method of testing bleach is a chemical one, such as is described on pages 79 and 80. The specific gravity also varies with the temperature, the higher the temperature the lower the reading. Hydrometers are usually graduated for use with liquids at 15° C. (60° F.), and only yield strictly accurate results at this temperature. In many cases hydrometers are graduated for special purposes; thus there is a glue tester which registers the percentage glue or gelatine in animal size. Sometimes the specific gravity is taken at a temperature considerably above 15° C., as in the case of the liquors obtained in soda recovery (p. 185). These liquors are thick or semi-solid at the ordinary temperature.

TABLE X.

Specific Gravities of Common Substances.

Agalite	2·69
Aluminium	2·67
,, oxide	3·9
,, sulphate (anhydrous salt)	2·7
Ammonia alum	1·63
Potash alum	1·72
Anthracite	1·3
Barium carbonate	4·3
,, chromate	4·5
,, oxide	5·4
,, sulphate (cryst.)	4·4
,, ,, (amorph.)	4·5
Brick	1·4-2·2
Brass	8·4-8·7
Calcium carbonate	2·7
,, oxide (quick lime)	3·2
,, silicate	2·8

TABLE X. (*continued*).

Calcium sulphate (anhydrous)	3·0
,, ,, (pearl hardening)	3·4
,, ,, (gypsum)	3·3
Chalk	2·5
Chrome alum (ammonia)	1·7
,, ,, (potash)	1·8
Cement	3·05
China clay (kaolin)	2·2
Charcoal (wood)	·3-·5
Copper	8·7-8·9
Clay	1·8-2·6
,, (for papermakers)	2·5-2·8
Fat (animal)	·92
Felspar	2·5-2·6
Fibre (cellulose)	1·5
Flint	2·7
Glass	2·4-3·4
Iron	6·6-7·9
,, oxide (ferric oxide)	5·1
,, carbonate	3·9
,, pyrites	4·6-5·2
Lead	11·3
,, oxide (litharge)	9·4
,, ,, (red lead)	9·0
,, chromate	6·3
,, carbonate	6·4
Magnesium oxide (calcined)	3·4
,, carbonate	2·8
Platinum	21·1
Porcelain	2·1-2·5
Potassium hydroxide (potash)	2·1
Quartz	2·7
Rosin (colophony)	1·06
Sand	1·4-1·6
Slate	2·7
Sodium hydroxide (caustic soda)	2·13
Steel	7·6-7·9
Sulphur	2
Tin	7·3
Talc	2·7
Wood—Ash	·84
,, Aspen	·60
,, Beech	·75-8·5
,, Bamboo	·31-·40
,, Boxwood	1·04
,, Elm	·55
,, Oak	·69-·99
,, Pine	·48-·70
,, Poplar	·39
,, Spruce	·48-·70
Zinc	6·8-7·2

TABLE XI.

COMPARISON OF DEGREES BAUMÉ AND TWADDELL WITH SPECIFIC GRAVITIES.

Degrees Baumé (B.).	Specific Gravity.	Twaddell (Tw.).
0	1·000	0
0·7	1·005	1
1·0	1·007	1·4
1·4	1·010	2
2·0	1·014	2·8
2·1	1·015	3
2·7	1·020	4
3·0	1·022	4·4
3·4	1·025	5
4·0	1·029	5·8
4·1	1·030	6
4·7	1·035	7
5·0	1·037	7·4
5·4	1·040	8
6·0	1·045	9
6·7	1·050	10
7·0	1·052	10·2
7·4	1·055	11
8·0	1·060	12
8·7	1·065	13
9·0	1·067	13·4
9·4	1·070	14
10·0	1·075	15
10·6	1·080	16
11·0	1·083	16·6
11·2	1·085	17
11·9	1·090	18
12·0	1·091	18·2
12·4	1·095	19
13·0	1·100	20
13·6	1·105	21
14·0	1·108	21·6
14·2	1·110	22
14·9	1·115	23
15·0	1·116	23·2
15·4	1·120	24
16·0	1·125	25
16·5	1·130	26
17·0	1·134	26·8
17·1	1·135	27
17·7	1·140	28
18·0	1·142	28·4
18·3	1·145	29
18·8	1·150	30
19·0	1·152	30·4
19·3	1·155	31
19·8	1·160	32
20·0	1·162	32·4
20·3	1·165	33
20·9	1·170	34
21·0	1·171	34·2
21·4	1·175	35
22·0	1·180	36
22·5	1·185	37
23·0	1·190	38
23·5	1·195	39
24·0	1·200	40
24·5	1·205	41
25·0	1·210	42
25·5	1·215	43
26·0	1·220	44
26·4	1·225	45
26·9	1·230	46
27·0	1·231	46·2
27·4	1·235	47
27·9	1·240	48
28·0	1·241	48·2
28·4	1·245	49
28·8	1·250	50
29·0	1·252	50·4
29·3	1·255	51
29·7	1·260	52
30·0	1·263	52·6
30·2	1·265	53
30·6	1·270	54

TABLE XI. *(continued)*.

Degrees Baumé (B.).	Specific Gravity.	Twaddell (Tw.).	Degrees Baumé (B.).	Specific Gravity.	Twaddell (Tw.).
31·0	1·274	54·8	43·8	1·435	87
31·1	1·275	55	44·0	1·438	87·6
31·5	1·280	56	44·1	1·440	88
32·0	1·285	57	44·4	1·445	89
32·4	1·290	58	44·8	1·450	90
32·8	1·295	59	45·0	1·453	90·6
33·0	1·297	59·4	45·1	1·455	91
33·3	1·300	60	45·4	1·460	92
33·7	1·305	61	45·8	1·465	93
34·0	1·308	61·6	46·0	1·468	93·6
34·2	1·310	62	46·1	1·470	94
34·6	1·315	63	46·4	1·475	95
35·0	1·320	64	46·8	1·480	96
35·4	1·325	65	47·0	1·483	96·6
35·8	1·330	66	47·1	1·485	97
36·0	1·332	66·4	47·4	1·490	98
36·2	1·335	67	47·8	1·495	99
36·6	1·340	68	48·0	1·498	99·6
37·0	1·345	69	48·1	1·500	100
37·4	1·350	70	48·4	1·505	101
37·8	1·355	71	48·7	1·510	102
38·0	1·357	71·4	49·0	1·515	103
38·2	1·360	72	49·4	1·520	104
38·6	1·365	73	49·7	1·525	105
39·0	1·370	74	50·0	1·530	106
39·4	1·375	75	50·3	1·535	107
39·8	1·380	76	50·6	1·540	108
40·0	1·383	76·6	50·9	1·545	109
40·1	1·385	77	51·0	1·546	109·2
40·5	1·390	78	51·2	1·550	110
40·8	1·395	79	51·5	1·555	111
41·0	1·397	79·4	51·8	1·560	112
41·2	1·400	80	52·0	1·563	112·6
41·6	1·405	81	52·1	1·565	113
42·0	1·410	82	52·4	1·570	114
42·3	1·415	83	52·7	1·575	115
42·7	1·420	84	53·0	1·580	116
43·0	1·424	84·8	53·3	1·585	117
43·1	1·425	85	53·6	1·590	118
43·4	1·430	86	53·9	1·595	119

TABLE XI. *(continued)*.

Degree Baumé (B.).	Specific Gravity.	Twaddell (Tw.).	Degrees Baumé (B.).	Specific Gravity.	Twaddell (Tw.).
54·0	1·597	119·4	60·9	1·730	146
54·1	1·600	120	61·0	1·732	146·4
54·4	1·605	121	61·1	1·735	147
54·7	1·610	122	61·4	1·740	148
55·0	1·615	123	61·6	1·745	149
55·2	1·620	124	61·8	1·750	150
55·5	1·625	125	62·0	1·753	150·6
55·8	1·630	126	62·1	1·755	151
56·0	1·635	127	62·3	1·760	152
56·3	1·640	128	62·5	1·765	153
56·6	1·645	129	62·8	1·770	154
56·9	1·650	130	63·0	1·775	155
57·0	1·652	130·4	63·2	1·780	156
57·1	1·655	131	63·5	1·785	157
57·4	1·660	132	63·7	1·790	158
57·7	1·665	133	64·0	1·795	159
57·9	1·670	134	64·2	1·800	160
58·0	1·671	134·2	64·4	1·805	161
58·2	1·675	135	64·6	1·810	162
58·4	1·680	136	64·8	1·815	163
58·7	1·685	137	65·0	1·820	164
58·9	1·690	138	65·2	1·825	165
59·0	1·691	138·2	65·5	1·830	166
59·2	1·695	139	65·7	1·835	167
59·5	1·700	140	65·9	1·840	168
59·7	1·705	141	66·0	1·842	168·4
60·0	1·710	142	66·1	1·845	169
60·2	1·715	143	66·3	1·850	170
60·4	1·720	144	66·5	1·855	171
60·6	1·725	145	66·7	1·860	172
			67·0	1·865	173

TABLE XII.

ACTUAL SPECIFIC GRAVITY CORRESPONDING TO THE CONTINENTAL AND AMERICAN BAUMÉ DEGREES (LUNGE).

Degrees.	Continental Baumé.	American Baumé.	Degrees.	Continental Baumé.	American Baumé.
1	1·007	1·005	34	1·308	1·309
2	1·014	1·011	35	1·320	1·317
3	1·022	1·023	36	1·332	1·334
4	1·029	1·029	37	1·345	1·342
5	1·037	1·036	38	1·357	1·359
6	1·045	1·043	39	1·370	1·368
7	1·052	1·050	40	1·383	1·386
8	1·060	1·057	41	1·397	1·395
9	1·067	1·064	42	1·410	1·413
10	1·075	1·071	43	1·424	1·422
11	1·083	1·086	44	1·438	1·441
12	1·091	1·093	45	1·453	1·451
13	1·100	1·100	46	1·468	1·470
14	1·108	1·107	47	1·483	1·480
15	1·116	1·114	48	1·498	1·500
16	1·125	1·122	49	1·514	1·510
17	1·134	1·136	50	1·530	1·531
18	1·142	1·143	51	1·540	1·541
19	1·152	1·150	52	1·563	1·561
20	1·162	1·158	53	1·580	1·573
21	1·171	1·172	54	1·597	1·594
22	1·180	1·179	55	1·615	1·616
23	1·190	1·186	56	1·634	1·627
24	1·200	1·201	57	1·652	1·650
25	1·210	1·208	58	1·671	1·661
26	1·220	1·216	59	1·691	1·683
27	1·231	1·231	60	1·711	1·705
28	1·241	1·238	61	1·732	1·727
29	1·252	1·254	62	1·753	1·747
30	1·263	1·262	63	1·774	1·767
31	1·274	1·269	64	1·796	1·793
32	1·285	1·285	65	1·819	1·814
33	1·297	1·293	66	1·842	1·835

CHAPTER III.

FUELS.

The commonest fuels are coal and coke, although petroleum, coal gas, suction gas, producer gas and Mond gas have also to be taken into consideration. The last four are, however, obtained indirectly from coal or coke.

Coal and Coke.—These substances are "impure" forms of carbon containing varying quantities of hydrogen, nitrogen, sulphur and other elements. Their value as fuel will depend chiefly upon the amount of heat they give out on burning, although there are other properties to be taken into consideration; thus, a coal with a fusible or partially fusible ash may cause an infinite amount of trouble, as the clinker will fuse and adhere to the fire bars; further, particles of unburnt coal will be retained by the clinker. Coals yielding a large percentage of ash are also of much less value, not only because combustible carbon is replaced by incombustible ash, but the ash retains particles of unburnt coal and hinders complete combustion of the whole of the carbon, choking up the fire bars. Much moisture in coal is also disadvantageous, not only because the more moisture the less coal, but this moisture has to be vapourised and converted into steam for which a definite amount of heat is required, which heat is withdrawn from serving a useful purpose. It will be seen that the more moisture and ash a fuel contains, the less combustible carbon and, therefore, the lower the heating value. On the other hand, a small amount of moisture is sometimes desirable, as it is said to promote combustion. The estimation of moisture, ash and calorific value will yield sufficient data on which to base an opinion of the value of the fuel. The figure for coking value or yield of carbonaceous matter obtained by gently igniting the coal in a crucible may also be determined.

Sampling.—If a piece of coal is picked out of a truckload and analysed, the figure obtained may or may not represent the average composition of the whole, as the composition of individual pieces will differ. The coal comprising the truckload may have come from different seams or different parts of the same seam, and the character and composition of coals always vary. Coal has been deposited by natural agencies and is therefore not uniform, but varies in composition like all other deposits.

Analyses will serve no good purpose unless an *average sample* of the whole consignment be taken. The necessity of this precaution cannot be too strongly emphasised. I have had samples of coal submitted for analysis where no sufficient precautions were taken to obtain a fair sample.

Methods of Sampling Coal.—It will often be found more difficult to obtain a fair average sample than to make the analysis. A convenient method to adopt is the following: A few shovelfuls are taken from different parts of the truck as it is discharged, or if the coal is conveyed to an overhead storage bin by an elevator a shovelful is taken every now and again from the buckets of the elevator and put together into a sack. In this way a hundredweight or so is collected and spread out on a clean, dry and impervious floor of stone, concrete or wood. It is then *thoroughly mixed* with a spade and made into a heap. If the lumps are large they must first be broken down somewhat, if possible, to the size of walnuts. The heap is then divided into four, as shown by the dotted lines in the illustration (fig. 10), and two of the quarters opposite one another, A and B, or C and D, are removed, leaving as little dust behind as possible; the remaining quarters are then thoroughly mixed, made into a heap, divided into four, two quarters removed, and the re-

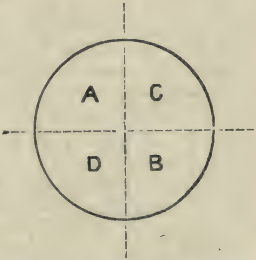


FIG. 10. — Diagram showing division of a heap in four quarters for purposes of sampling.

mainder mixed and treated as before. These operations are repeated until twenty or thirty pounds remain. At this stage the lumps must be further crushed so as to obtain the coal in small pieces of a uniform size, certainly not larger than walnuts. The quartering and mixing are repeated two or three times, and the remainder, amounting to a pound or two, with all the dust and fine powder properly belonging to it, is taken to the laboratory where it is further crushed to a coarse powder by putting it through a coffee mill which should be kept for the purpose, or crushing in a mortar. The operation of quartering and mixing is now repeated with the crushed powder on a clean sheet of newspaper until only 100 or 200 grams remain. This is ground to a fine powder in a mortar, and then quartered and mixed, as before, to reduce it to 20 or 30 grams, which is amply sufficient for analysis. It should be transferred immediately to a small stoppered bottle.

Moisture.—Two or three grams of the finely-powdered substance are weighed out on to a large watch glass and spread over it in a thin layer. It is then dried in an air-bath, or, better, a steam-jacketed oven, as the temperature must not be allowed to rise above 110° C. The watch glass with contents are weighed every half-hour until the weight is constant or begins to increase. The minimum weight is taken as that of the dry substance. The glass and contents should be allowed to cool down in a desiccator before weighing, in order that the coal may not have an opportunity of absorbing moisture from the air. The weighing should be done as soon as practicable after the glass and contents are cold, as the air in a desiccator is never quite dry if the cover is frequently removed.

The loss in weight on drying gives the moisture (hygroscopic water), which should be calculated and expressed as percentage on the original weight of the coal. The figures obtained vary considerably for different coals; they seldom exceed 10 per cent., and for Welsh coals are generally less than 2 per cent.

Ash.—Weigh out one to two grams of finely-powdered coal into a platinum crucible, which should be supported in an inclined or almost horizontal position on a clay triangle. The crucible is very gradually heated by a small flame, which should be at such a distance that it does not play on the crucible. In this manner the coal is gradually burnt away, leaving the ash. The flame should not be turned on full or allowed to play on the crucible till near the end of the operation, as the ash of many coals tends to fuse and enclose portions of carbon, which are never completely burnt up however long the crucible is heated. This results in too high a figure for ash. It takes some time to burn coal to an ash with a low flame, but once having arranged the crucible and burner underneath, it requires no further attention till combustion is complete. Special attention should be paid to the nature of the ash, as a coal with an easily-fusible ash gives no end of trouble by fusing on to and choking the fire bars, from which it is troublesome and difficult to remove.

The ash of coal is seldom white, but reddish-brown in colour from the iron it contains. This has its origin in the pyrites and sulphur compounds found even in the best coals.

When the crucible and ash have been weighed, and no further loss in weight occurs on reheating, a little alcohol should be poured into the crucible when the light particles of ash are easily suspended and may be removed by carefully decanting, while any particles of unburnt coal will be seen at the bottom. In this manner any unburnt residue of coal or coke is easily detected, in which case, needless to say, another determination of the ash must be made. As before, the ash is expressed as a percentage of the weight of the original coal. It varies enormously in coal from different sources; 4 or 5 per cent. may be taken as a rough average figure for good coals.

Calorific Value.—The unit commonly employed in this country to express the calorific value is the British thermal unit, written B.T.U., which is the amount of heat required to raise one pound of water 1° Fahrenheit. The unit in vogue on the Continent and also used for scientific work in this country is the "calorie," in which the Centigrade thermometric scale is used instead of the Fahrenheit, and the gram taken as the unit in the place of the pound, the calorie being the amount of heat required to raise 1 gram of water 1° Centigrade. As a Fahrenheit degree is equal to $\frac{5}{9}$ of a Centigrade degree, the calorific value expressed in calories per gram is easily converted into British thermal units per pound by multiplying by $\frac{9}{5} \times 453 \cdot 6$.

It is best in all cases to work with the centigrade scale and obtain the result in calories, afterwards converting this figure into British thermal units if desired.

The apparatus employed for determining the calorific value of a fuel, termed a calorimeter, consists of a chamber in which a weighed quantity of the fuel is burnt surrounded by and immersed in a vessel of water to which the heat developed in the chamber is communicated. The vessel of water is fitted with a sensitive thermometer, so that the rise in temperature brought about by burning the fuel may be measured. Knowing the quantity of water (in c.c.) in the vessel, and multiplying this by the rise of temperature in degrees centigrade, we have at once the number of calories produced by the combustion of the fuel, which is calculated to 1 gram as a convenient basis for purposes of comparison. Some heat is absorbed by the combustion chamber and outer vessel, and some lost by radiation, for which an allowance must be made. It is usual to express this in terms of the number of grams of water which would absorb the same amount of heat, and which for our purpose may be regarded as thermally equivalent. This figure, known as the "water equivalent," must of course be added to the weight of water in the outer vessel, in order to arrive at a fair estimate of the total heat absorbed, and therefore liberated by the fuel when burnt.

A calorimeter must be so constructed and worked that combustion is complete. There must not be any residue of unburnt carbon. All modern calorimeters are so arranged that the fuel is burnt in oxygen gas; either the coal is ignited electrically in compressed oxygen contained in a strong iron vessel, or it is burnt in a stream of oxygen at the ordinary atmospheric pressure, the gas and products of combustion parting with their heat as they escape bubbling through the water in the calorimeter.

The former type or bomb calorimeter is best adapted for accurate work, but is a very expensive instrument. For most purposes the latter type is sufficiently accurate. I shall not, therefore, describe the bomb calorimeter but pass at once to the second form, of which Darling's may serve as an example.

DARLING'S CALORIMETER.

This is shown in figures 11 and 12, and consists of a support "A" carrying a small platinum crucible "C," in which the sample of fuel is placed. It may be ignited either electrically by connecting the wires "P" and "Q" to a battery, or in a simpler manner, which also works well, by placing a few grains of powdered sulphur on the top of the coal and igniting the sulphur with a piece of red-hot wire and rapidly replacing the cork. The oxygen is introduced at "O" by connecting with an oxygen cylinder, and is conducted on to the surface of the fuel. This tube may be raised or lowered during the burning, and, being held in position by an elastic rubber stopper, it may be directed on to any particular part of the fuel in order to ensure complete combustion. The oxygen and products of combustion pass down through

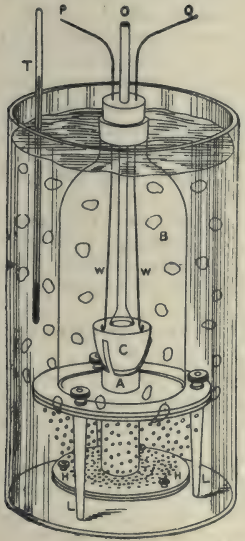


FIG. 11.

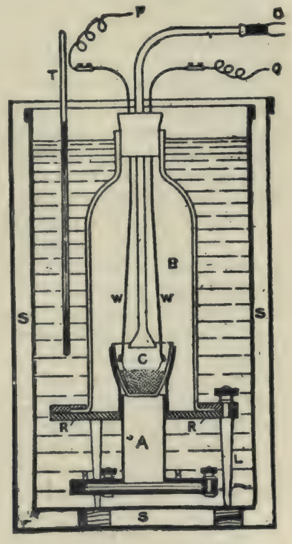


FIG. 12.

"A" and out between plates "HH," bubbling up through the water. When the combustion is complete a slow current of gas is allowed to pass until the temperature, as indicated by the thermometer T, has reached its maximum, or the bell-jar may be flooded by disconnecting the tube "O," and the whole liquid mixed up by raising and lowering it a few times.

The following are instructions for working the instrument (*Engineering*, 20th June, 1902):—

1. Carefully grind up an average sample in an iron mortar, and weigh out 1 to 1·5 grains in the crucible. Brush any particles from the sides into the mass at the bottom.

2. Prepare a quantity of water at a temperature about 2·5° C. below the temperature of the room. Water drawn from a tap varies in temperature according to the season; but usually it will be necessary to add a little warm water to it in order to bring it to the requisite temperature. Measure out 1400 c.c. into the vessel.

3. Place the crucible in position, and fasten the glass cover down upon the rubber ring by means of the screws, so as to form an air-tight joint. The screws must only be turned until a resistance is felt; any further tightening might crack the glass cover.

4. Insert the rubber cork into the neck so that the ignition wire is embedded in the fuel. The copper wires should terminate about level with the rim of the crucible, and the tube delivering the oxygen about half an inch above the surface of the fuel.

5. Turn on a gentle stream of oxygen from a cylinder or gasholder, and immerse the apparatus in the water. Carefully note the temperature of the water and complete the battery circuit. As soon as the fuel is ignited, disconnect the battery. Allow the combustion to proceed steadily until completed, then continue passing the oxygen, mixing the water by lifting the combustion arrangement up and down until no further rise of temperature is observed. Note the temperature carefully.

Precautions:—

(*a*) The oxygen must never be admitted so rapidly as to cause particles to be blown out of the crucible. The time required to burn 1 gram of average coal in a steady stream of oxygen is about 4·5 minutes.

(*b*) If the sample is observed to burn with a smoky flame, the combustion must be stopped, as the result will be valueless owing to unburnt carbon. In such cases the fuel must be mixed before combustion with $\frac{1}{3}$ its weight of dried kaolin or calcined alumina; or more if found necessary. This will ensure smokeless burning without interfering with the heat evolved.

(*c*) During the combustion the tube delivering the oxygen should be moved about so as to ensure that every particle of coal is burnt. The flexibility of the rubber cork allows of this operation being easily performed. This precaution is especially necessary when a porcelain crucible is used. A platinum crucible is preferable, and is not injured by the combustion. Being a better conductor of heat than porcelain, every particle of fuel in contact with the platinum crucible is more readily raised to its ignition point. Nickel crucibles are well adapted for the purpose.

6. The calorific value is calculated as follows:—

$$\frac{(\text{Weight of water} + \text{water equivalent}) \times \text{rise of temperature}}{\text{Weight of fuel taken}}$$

(The figure expressing "water equivalent" of the calorimeter and vessel is furnished with the apparatus. It is the weight of water which would absorb the same amount of heat as the apparatus.)

One cubic centimeter of water is taken as weighing 1 gram. If a Fahrenheit thermometer is used, the result will be expressed as British thermal units (per lb. of fuel); if centigrade readings are taken, the figure will represent calories (per gram of fuel).

Example.—One gram of coal burnt as above:—

Water taken = 1400 c.c. or grams.
Water equivalent of apparatus and vessel = 230 grams.
Temperature of water before combustion = 13·4° C.
Temperature of water after combustion = 17·3° C.
Temperature of room = 16·3° C.
Calorific value =

$$\frac{(1400 + 230) \times 17{\cdot}3 - 13{\cdot}4}{1} = 6357 \text{ calories (per gram), or}$$

$$6357 \times \tfrac{9}{5} = 11{,}443 \text{ British thermal units (per lb.).}$$

Evaporative Power of Fuels.—On burning a gram of pure carbon (wood charcoal) to carbon dioxide gas, some 8080 calories are liberated or expressed in the customary British units (1 lb. of wood charcoal produces 14,544 B.T.U.), and as 1 gram of water at 100° C. requires 537 calories to convert it into steam at the same temperature, it follows that these 8080 calories will convert $\frac{8080}{537} = 15$ grams of water into steam, or expressed in lbs., 1 lb. of carbon will convert 15 lb. of water at 100° C. into steam at the same temperature. If we take water at 15° C. instead of 100° C., the amount of heat required to convert it into steam is of course greater, so that only some 13 lb. of water will be evaporated by the heat liberated by burning one 1 lb. of carbon.

It is necessary to bear these relations in mind, as the heating power of a fuel is sometimes expressed as evaporative power, that is to say, as the number of lbs. of water converted into steam both at 100° C. and at atmospheric pressure by 1 lb. of fuel. To convert the figures obtained for calorific value expressed in B.T. units into the corresponding figures for evaporative power, it is only necessary to divide by 966, or, if expressed in gram calories, by 537. Thus, taking the example given above, the evaporative power is $\frac{11443}{966} = \frac{6357}{537} = 11{\cdot}8$.

Of course the amount of water actually evaporated in a steam boiler is much less than this, and is dependent upon the efficiency of the boiler. In the first place, the feed-water has to be heated from a low temperature to somewhat above 100° C., the temperature of the water and steam in the boiler. Secondly, much heat is lost by radiation from the surface of the boiler. For rough purposes we may say that only two-thirds of the heat evolved by the burning fuel is available for converting water into steam, one-third being lost by radiation and in other ways. The accompanying table (page 43), taken from the analyses of Delabéche and Playfair, gives the ash, calorific value and evaporative power calculated from the calorific value, as well as the actual evaporative power as measured in boiler trials.

It is evident from what has already been said that, speaking broadly, the larger the percentage of moisture and ash, the less carbon and, therefore, the lower the calorific value and evaporative power of the coal.

Having now determined the relative efficiency of a number of fuels, it remains to take the price into consideration in order to decide which of them would be the most economical to use. This is merely a matter of arithmetic; the simplest method being to calculate what would be the cost of sufficient of the different samples to produce the same amount of heat. Thus, supposing we desire to compare the price of two coals, one at 12s. and the other at 14s. per ton, whose calorific values are respectively 10,920 and 13,200 B.T.U. The amount of heat liberated by 1 ton of coal at 14s. is 13,200 × 2240 B.T.U., and therefore the cost of sufficient of the cheaper coal to liberate the same amount of heat will be 12s. × $\frac{13200}{10920}$ = 14·505, approximately 14s. 6d. In other words, a saving of 6d. per ton will be effected by using the higher-priced coal.

TABLE XIII.

Calorific Value of Coals.

Coals.	Ash.	Calorific Value in B.T.U.	Evaporative Power as Calculated.		Evaporative Power (as Determined in Boiler Trials).
			From Water at 62°.	From Water at 212°.	
		Units.	Pounds.	Pounds.	Pounds.
Welsh . .	4·91 %	14,858	13·46	15·52	9·05
Newcastle .	3·77 %	14,820	13·29	15·32	8·01
Derbyshire and Yorkshire .	2·65 %	13,860	12·43	14·34	7·58
Lancashire .	4·88 %	13,918	12·62	14·56	7·94
Scotch . .	4·03 %	14,164	12·75	14·77	7·70
Average of Samples .	4·05 %	14,320	12·83	14·82	8·13
Anthracite .		13,302	12·55	14·50	9·85

This is the most reliable method of calculating the value of a coal unless an actual boiler trial be made. The latter may be necessary, as the choice of a fuel depends partly on the particular boiler and furnace for which it is required.

TABLE XIV.

Comparison of Different Thermometric Scales.

Centigrade.	Reamur.	Fahrenheit.	Centigrade.	Reamur.	Fahrenheit.
200	160	392	160	128	320
199	159·2	390·2	159	127·2	318·2
198	158·4	388·4	158	126·4	316·4
197	157·6	386·6	157	125·6	314·6
196	156·8	384·8	156	124·8	312·8
195	156	383	155	124	311
194	155·2	381·2	154	123·2	309·2
193	154·4	379·4	153	122·4	307·4
192	153·6	377·6	152	121·6	305·6
191	152·8	375·8	151	120·8	303·8
190	152	374	150	120	302
189	151·2	372·2	149	119·2	300·2
188	150·4	370·4	148	118·4	298·4
187	149·6	368·6	147	117·6	296·6
186	148·8	366·8	146	116·8	294·8
185	148	365	145	116	293
184	147·2	363·2	144	115·2	291·2
183	146·4	361·4	143	114·4	289·4
182	145·6	359·6	142	113·6	287·6
181	144·8	357·8	141	112·8	285·8
180	144	356	140	112	284
179	143·2	354·2	139	111·2	282·2
178	142·4	352·4	138	110·4	280·4
177	141·6	350·6	137	109·6	278·6
176	140·8	348·8	136	108·8	276·8
175	140	347	135	108	275
174	139·2	345·2	134	107 2	273·2
173	138·4	343·4	133	106·4	271·2
172	137·6	341·6	132	105·6	269·6
171	136·8	339·8	131	104·8	267·8

TABLE XIV. (*continued*).

Centigrade.	Reamur.	Fahrenheit.	Centigrade.	Reamur.	Fahrenheit.
170	136	338	130	104	266
169	135 2	336·2	129	103·2	264·2
168	134·4	334·4	128	102·4	262·4
167	133·6	332·6	127	101·6	260·6
166	132·8	330·8	126	100·8	258·8
165	132	329	125	100	257
164	131·2	327·2	124	99·2	255·2
163	130·4	325·4	123	98·4	253·4
162	129·6	323·6	122	97·6	251·6
161	128·8	321·8	121	96·8	249·8
120	96	248	80	64	176
119	95·2	246·2	79	63·2	174·2
118	94·4	244·4	78	62·4	172·4
117	93·6	242·6	77	61·6	170·6
116	92·8	240·8	76	60·8	168·8
115	92	239	75	60	167
114	91·2	237·2	74	59·2	165·2
113	90·4	235·4	73	58 4	163 4
112	89·6	233·6	72	57·6	161·6
111	88·8	231·8	71	56·8	159·8
110	88	230	70	56	158
109	87·2	228·2	69	55·2	156·2
108	86·4	226·4	68	54·4	154·4
107	85·6	224·6	67	53·6	152·6
106	84·8	222·8	66	52·8	150·8
105	84	221	65	52	149
104	83·2	219·2	64	51·2	147·2
103	82·4	217·4	63	50·4	145·4
102	81·6	215·6	62	49·6	143·6
101	80·8	213·8	61	48·8	141·8
100	80	212	60	48	140
99	79·2	210·2	59	47·2	138·2
98	78·4	208·4	58	46·4	136·4
97	77·6	206·6	57	45·6	134·6
96	76·8	204·8	56	44·8	132·8
95	76	203	55	44	131
94	75·2	201·2	54	43·2	129·2
93	74·4	199·4	53	42·4	127·4
92	73·6	197·6	52	41·6	125·6
91	72·8	195·8	51	40·8	123·8

TABLE XIV. (*continued*).

Centigrade.	Reamur.	Fahrenheit.	Centigrade.	Reamur.	Fahren heit.
90	72	194	50	40	122
89	71·2	192·2	49	39·2	120·2
88	70·4	190·4	48	38·4	118·4
87	69·6	188·6	47	37·6	116·6
86	68·8	186·8	46	36·8	114·8
85	68	185	45	36	113
84	67·2	183·2	44	35·2	111·2
83	66·4	181·4	43	34·4	109·4
82	65·6	179·6	42	33·6	107·6
81	64·8	177·8	41	32·8	105·8
40	32	104	20	16	68
39	31·2	102·2	19	15·2	66·2
38	30·4	100·4	18	14·4	64·4
37	29·6	98·6	17	13·6	62·6
36	28·8	96·8	16	12·8	60·8
35	28	95	15	12	59
34	27·2	93·2	14	11·2	57·2
33	26·4	91·4	13	10·4	55·4
32	25·6	89·6	12	9·6	53·6
31	24·8	87·8	11	8·8	51·8
30	24	86	10	8	50
29	23·2	84·2	9	7·2	48·2
28	22·4	82·4	8	6·4	46·4
27	21·6	80·6	7	5·6	44·6
26	20·8	78·8	6	4·8	42·8
25	20	77	5	4	41
24	19·2	75·2	4	3·2	39·2
23	18·4	73·4	3	2·4	37·4
22	17·6	71·6	2	1·6	35·6
21	16·8	69·8	1	0·8	33·8
			0	0	32

CHAPTER IV.

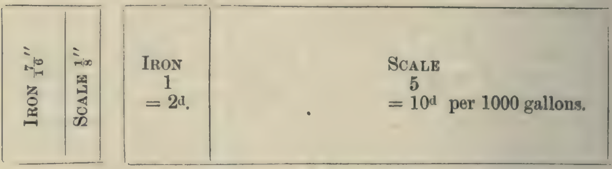
WATER.

When it is remembered that every pound of paper comes into contact with 50 to 100 gallons of water in the course of manufacture, and that the substances normally present dissolved in water have a considerable influence on the colouring and sizing of pulp, the fibres and properties of the paper generally, no apology is needed for devoting a chapter to the examination of water and methods of analysing it.

Too little attention has hitherto been given to this matter, the papermaker being quite content if his water be bright and clear and the supply sufficient for his purpose. Yet the dissolved solids found in all waters influence the manufacturing operations in no small degree. It is, for instance, extremely difficult to make a good blotting which does not lose its absorbency when in use if the water supplied is very hard. This will be referred to later. Again, in engine sizing the dissolved solids profoundly influence the action of the rosin, size and alum. The concentration of pulp in the beater is, say, 5 per cent., or about 3 lb. to the cubic foot, in other words, a beater taking 2 cwts. of dry rag will require 448 gallons of water. It is no unusual thing in many districts for the water to contain 20 grains of temporary hardness (carbonates of calcium and magnesium) per gallon, so that every ton of rags will be brought into contact with 20 × 4480 = 89600 grains, or nearly 13 lb. of calcium carbonate, which will require about 14 lb. of alum to react with it. This alum is simply wasted ; used up without having produced any effect on sizing the paper. It partially accounts for the fact that the papermaker has to add far more alum than should be theoretically required for reacting with the rosin size.

The matter, however, does not end here, as even after sufficient additional alum has been added there is still the influence of the dissolved solids on the manner in which the rosin size is precipitated by the alum.

Leaving the actual operations in the mill, there is also the question of steam-raising to be considered. Few mills in this country are independent of the steam boiler, and the presence of much hardness soon makes itself apparent by the formation of sludge and scale in the boiler. If the water happens to contain much permanent hardness, the scale, consisting of calcium sulphate, is generally very hard and difficult to get rid of without damaging the boiler plates, and if not removed there is a tremendous loss of efficiency quite apart from danger of explosion.



ACTUAL THICKNESS OF BOILER PLATE AND SCALE.

COMPARATIVE RESISTANCE TO PASSAGE OF HEAT AND COST.

FIG. 13.—Relative Resistance of Boiler Plate and Boiler Scale to Passage of Heat (after Collet).

This loss of efficiency is seldom adequately realised. The resistance to the passage of heat of calcium carbonate (chalk) is seventeen times, and of calcium sulphate (sulphate of lime) is forty-eight times as great as that of wrought iron. This is graphically shown in fig. 13, where the relative thicknesses and resistance to heat are placed side by side.

It will be seen that a scale $\frac{1}{8}$ inch thick occasions five times as much loss as a boiler plate $\frac{9}{16}$ inch thick. Taking coal at 13s. the ton, about half a ton, 7s. 6d. worth, will be required to evaporate 1000 gallons in a good boiler, so that we may reckon an additional cost of 10d. per 1000 gallons, or 1s. 8d. per ton of coal for every $\frac{1}{8}$ inch of a scale on the furnace plates. As Collett remarks, many waters are dear at 1d. per 1000 gallons while others are cheap at 1s.

Water supplies, especially surface and river water, may contain suspended matter as well as dissolved solids, and for the manufacture of fine papers the suspended matter must be removed. For this purpose there are a number of automatic filtering appliances on the market. Some account of these self-cleansing filters will be found at the end of this chapter. To examine the suspended matter some of the water is drawn off into a clear glass cylinder and set aside to stand. If the particles in suspension settle rapidly and completely, they probably consist entirely of mineral matter, but if slowly, taking a day or two for the water to clear, the suspended particles consist largely of organic matter. A little of the sediment examined under the microscope will also help to ascertain its nature. If the amount of suspended matter is small, allow a liter of the water to stand till the sediment has deposited, and carefully decant as much as possible of the clear liquid, taking the remainder with the sediment for the analysis. If the quantity of suspended matter is large, take straight away 100 c.c., or if need be less. Fold two similar filter papers, place one on each pan of the balance and cut away the apex of the heavier with a pair of scissors till they counterpoise each other. Place the uncut paper inside the cut one, and both in a funnel for filtering in the usual manner. Shake up the water and pour through the double filters, so that the suspended matter is caught in the inner filter paper, but both are wetted. Get the whole of the suspended matter on to the paper, and dry together in air bath at 110° C., and weigh the contents of the inner paper by using the outer cut one as a counterpoise in the other pan.

The paper containing the sediment is now ignited in a tared platinum crucible; the weight, after deducting the weight of the crucible and the ash of the filter paper, gives the ash of the sediment or mineral matter it contains. The figure so obtained will be rather less than the actual mineral matter in suspension, as water of constitution and carbon dioxide gas still held at 110° C. will be driven off on ignition. This, however, cannot be allowed for. On subtracting the weight of the mineral matter from the total weight of the suspended matter, the weight of the organic matter in suspension is obtained. The results are conveniently expressed in parts per 100,000 or in grains per gallon (parts per 70,000) as is done in water analysis generally.

Some waters deposit solid matter from solution on standing from loss of part of the carbonic acid they originally contained. In virtue of this they hold calcium, magnesium and iron in solution as bicarbonates, the water should not, therefore, be set aside too long before analysing. The iron is generally held as ferrous bicarbonate, and is deposited not so much from loss of carbon dioxide, but from oxidation of the ferrous iron to the ferric state. The method for estimating iron in solution is given later on in this chapter ; the ash of the sediment may be digested with a little pure nitric acid, and also tested for iron with potassium ferro-cyanide solution. The dissolved solids cannot be removed mechanically, but chemical means must be adopted as well as mechanical appliances. Before discussing the various plant which may be required it will be necessary to consider the cause of hardness and the methods of testing hard water.

Hardness is caused by the dissolved solids, and is of two kinds : temporary and permanent.

Temporary hardness is due to the presence of the bicarbonates of calcium and magnesium ; on boiling, these are decomposed, carbon dioxide driven off and the carbonates precipitated.

$$\underset{\substack{\text{Soluble}\\\text{calcium}\\\text{bicarbonate.}}}{CaH_2(CO_3)_2} = \underset{\substack{\text{Insoluble}\\\text{calcium}\\\text{carbonate.}}}{CaCO_3} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2} + \underset{\text{Water.}}{H_2O.}$$

Permanent hardness is due to sulphates and chlorides of calcium and magnesium, and is not affected by boiling. For domestic purposes water is softened with soda or soap. In the latter case a sodium salt of stearic and other acids is formed, which reacts with the lime and magnesia in solution to give insoluble lime and magnesium stearates (curdy precipitates), leaving the water soft (free from dissolved solids). When sufficient soap has been added to react with all the calcium and magnesium salts in solution, the smallest excess will produce a lather. With insufficient soap no lather is formed. The chemist by measuring the soap required to produce a lather with a given quantity of water can determine the amount of salts in solution, or, in other words, the *total hardness* of the water, which includes both the *temporary* and *permanent* hardness mentioned above.

Clark's Soap Test.—Before making up the standard soap solution required in this test it will be necessary to prepare, artificially, a water of known hardness against which to standardise the soap solution. For this purpose a solution of calcium chloride is prepared by weighing out ·2 grams of pure carbonate of calcium. It is best to use either the pure precipitated substance or the crystalline mineral known as calcspar. It is dissolved with dilute hydrochloric acid in a small vessel kept covered with a clock glass, every precaution being taken to prevent loss through spurting. The solution is evaporated to dryness on the water bath, then taken up with a little fresh distilled water and again dried down to drive off every trace of acid. The neutral solution of calcium chloride is finally made up to 1 liter. To prepare the standard soap solution procure some genuine Castile soap, and slice up about 100 grams into thin shavings; then macerate with rectified spirit, and, when most of the soap is dissolved, filter through a dry paper. This solution is then diluted with a mixture of two parts of spirit and one of water. After standing for a few days, measure out 50 c.c. of the standard calcium chloride solution into an 8 or 10 oz. white glass-stoppered bottle; put the soap solution in a burette and run in 1 c.c. at a time into the bottle, shaking vigorously after each addition. A point will eventually be reached when more than sufficient soap has been added to react with the calcium chloride, and the excess forms a lather which is permanent on standing for five minutes, that is to say, covers the whole surface without a break. The sound and feel when shaking the bottle should be noted, as the shock is less violent and the sound softer as soon as an excess of soap has been added; 14·25 c.c. of soap solution should be required for 50 c.c. of standard calcium chloride, which is equivalent to 20 parts of carbonate of calcium per 100,000 of water. If stronger than this, the soap solution must be further diluted and retested till correct. The standard soap solution is then ready.

In testing a sample of water it is easy to calculate the hardness from the number of c.c. of soap solution required by making use of the table given below.

TABLE XV.

Hardness Table.

Parts of $CaCO_3$ per 100,000.

c.c. of Soap Solution.	Parts of $CaCO_3$.	c.c. of Soap Solution.	Parts of $CaCO_3$.
0·7	·00	·1	·14
·8	·16	·2	·29
·9	·32	·3	·43
1·0	·48	·4	·57
·1	·63	·5	·71
·2	·79	·6	·86
·3	·95	·7	7.00
·4	1·11	·8	·14
·5	·27	·9	·29
·6	·43	6·0	·43
·7	·56	·1	·57
·8	·69	·2	·71
·9	·82	·3	·86
2·0	·95	·4	8·00
·1	2·08	·5	·14
·2	·21	·6	·29
·3	·34	·7	·43
·4	·47	·8	·57
·5	·60	·9	·71
·6	·73	7·0	·86
·7	·86	·1	9·00
·8	·99	·2	·14
·9	3·12	·3	·29
3·0	·25	·4	·43
·1	·38	·5	·57
·2	·51	·6	·71
·3	·64	·7	·86
·4	·77	·8	10·00
·5	·90	·9	·15
·6	4·03	8·0	·30
·7	·16	·1	·45
·8	·29	·2	·60
·9	·43	·3	·75
4·0	·57	·4	·90
·1	·71	·5	11 05
·2	·86	·6	·20
·3	5·00	·7	·35
·4	·14	·8	·50
·5	·29	·9	·65

TABLE XV. (*continued*).

c.c. of Soap Solution.	Parts of $CaCO_3$.	c.c. of Soap Solution.	Parts of $CaCO_3$.
·6	·43	9·0	·80
·7	·57	·1	·95
·8	·71	·2	12·11
·9	·86	·3	·26
5·0	6·00	·4	·41
·5	·56	·8	·70
·6	·71	·9	·86
·7	·86	13·0	18·02
·8	13·01	·1	·17
9	·16	·2	·33
10·0	·31	·3	·49
·1	·46	·4	·65
·2	·61	·5	·81
·3	·76	·6	·97
·4	·91	·7	19·13
·5	14·06	·8	·29
·6	·21	·9	·44
·7	·37	14·0	·60
·8	·52	·1	·76
·9	·68	·2	·92
11·0	·84	·3	20·08
·1	15·00	·4	·24
·2	·16	·5	·40
·3	·32	·6	·56
·4	·48	·7	·71
·5	·63	·8	·87
·6	·79	·9	21·03
·7	·95	15·0	·19
·8	16·11	·1	·35
·9	·27	·2	·51
12·0	·43	·3	·68
·1	·59	·4	·85
·2	·75	·5	22·02
·3	·90	·6	·18
·4	17·06	·7	·35
·5	·22	·8	·52
·6	·38	·9	·69
·7	·54	16·0	·86

NOTE.—To convert parts per 100,000 to grains per gallon multiply by ·7.

Unfortunately, the method is not an exact one, and can only be relied upon when the same conditions are preserved in all tests. It will, however, be found very convenient for rough tests, especially when it is desired merely to check from time to time the efficiency of water-softening plant. It can also be applied to distinguish between "temporary" and "permanent" hardness in a sample of water. 50 c.c. of the latter are taken and boiled for half an hour in an open vessel, by which means the "temporary hardness" is precipitated; the liquid is poured through a dry filter paper and titrated with soap solution as before; the result gives the "permanent hardness" (sulphates). By subtracting the "permanent" from the "total" hardness, we obtain the "temporary" hardness. This latter figure may be checked by merely titrating the water with standard acid in the presence of methyl orange, provided the water has not an alkaline reaction. Decinormal acid may be used, and if possible a fairly large quantity, say 500 c.c. of water. Every c.c. of standard acid required will then be equivalent to one part of calcium carbonate per 100,000. This titration is easy and accurate, and is the simplest means of getting at the "temporary hardness."

To accurately estimate the permanent hardness it is best to determine the sulphates as sulphuric acid. At least 500 c.c. of water are concentrated in a porcelain dish with a few c.c. of hydrochloric acid, until the volume of the liquid is reduced to 100 to 200 c.c. It is then transferred to a beaker, and the sulphates precipitated in the hot liquid with a solution of barium chloride exactly as described for alum (p. 89).

On reference to Table VII. (p. 22) the factor for conversion of barium sulphate to sulphuric acid, calcium sulphate or carbonate may be found according to the form in which it is desired to express the permanent hardness.

I have spoken of hardness as parts of calcium carbonate per 100,000. However, hardness sometimes is reckoned in grains per gallon, and as there are 70,000 grains to the gallon, 1 grain per gallon is equivalent to 1 part per 70,000. The conversion of one into the other is obviously a matter of simple calculation.

Another point requires explanation. It has been stated that besides calcium, we have magnesium carbonate, and not only carbonates but sulphates, occurring naturally in water. In reckoning the total hardness, therefore, all these substances are reckoned as calcium carbonate, that is to say, calculated to the equivalent amount of calcium carbonate.

Total Solids.—It is usual to determine the total amount of solid matter in solution by evaporating down a quantity of water, preferably in a platinum dish, drying at 100° C. and weighing. The figure obtained is useful as giving an idea of the general purity of water. If the results are required in grains per gallon, it will be convenient to take 70 c.c., or some simple multiple of this number, but if in parts per 100,000, 100 c.c. or larger quantities.

Mineral Analysis.—Where exact information is necessary, as, for instance, in calculating the quantity of chemical required for softening water, it is much better to make a mineral analysis of the more important constituents than to depend on titrations with soap solution. The most important constituents to determine are calcium and magnesium carbonates, sulphates, chlorides and silica, for details of which reference should be made to a text-book on quantitative analysis. A water containing considerable quantities both of magnesium and chlorine is unsuitable for boiler purposes, as hydrochloric acid is formed in the boiler owing to the decomposition of magnesium chloride.

There is one other constituent of considerable importance from the papermaker's point of view, and that is the iron. Even small quantities of iron may lower the colour of high-class papers, so that its estimation is of importance not only in water but in alum and other chemicals with which the pulp or paper may come in contact. The method, which is substantially the same in all cases, will be described here. It depends upon the formation of Prussian blue by the action of potassium ferrocyanide on the iron which must be converted into the ferric state.

A standard solution of ferric iron may be conveniently made of ·01 per cent. strength by weighing out ·7 gram of ferrous ammonium sulphate (which contains $\frac{1}{7}$ of its weight of iron), dissolving in a small quantity of water in a dish, adding 1 c.c. of nitric acid (free from iron) and warming gently on a water bath in order to oxidise the ferrous iron to the ferric state. The solution is then made up to 1000 c.c. in a measuring flask, so that each c.c. is equivalent to ·0001 gram iron. Waters containing large quantities of iron give a perceptible coloration with ferrocyanide of potassium, but it is usually necessary to evaporate 500 c.c. of the water under examination to dryness after adding a few drops of nitric acid (free from iron) for the same purpose as before, when it is desired to estimate the quantity of iron present. Transfer to a 50 c.c. Nessler glass, and make up to the mark with distilled water. Now take a similar Nessler glass and run into it a couple of c.c. of standard iron solution from a burette and fill the glass up to the mark with water.

Place the glasses side by side on a sheet of white paper or white glazed tile, and add to each a couple of c.c. of a freshly prepared dilute solution of potassium ferrocyanide, and compare the depths of shade of the blue colours developed. If they be of unequal shade a fresh standard is made up, measuring out a smaller or larger quantity of the standard iron as the case may be. Supposing that 3·3 c.c. were required, this would mean that 500 c.c. of water contained 3·3 × ·0001 gram of iron, or ·000066 per cent. It is, however, more usual in the case of water to express the amount of iron in parts per 100,000 or grains per gallon, which in this case would be ·066 part per 100,000, or $\cdot066 \times \frac{7}{10} = \cdot0462$ grain per gallon.

The proportion of iron which is allowable for high-class papers, such as hand-made and the best rag papers, may be put at 7 to 20 parts per 100,000, the latter may be taken as the limit. If stored in tanks the water should be tested as it leaves the tanks, as they are liable to rust, and iron may be dissolved in this way and contaminate the paper.

Water Purification.—Water for industrial purposes often requires to be purified, and the sort of purification will depend upon the purpose for which it is intended. For the manufacture of paper and pulp a water of a high degree of purity is generally necessary. To remove the suspended matter filtration is required, and there are several types of filters. In other cases, especially if a peaty water has to be dealt with, it is advantageous to treat with aluminoferric or other form of crude sulphate of alumina, the quantity depending upon the contamination of the water. One to two tons to the ten million gallons may be taken as an average. After treatment the water is passed through settling tanks, and is then ready for use.

Water Softening.—This is the treatment which is most often applied for the purification of water for steam raising, and it is generally necessary to remove both temporary and permanent hardness. The process universally adopted for removal of the former is treatment with lime, either in the form of lime water, that is, a clear solution of calcium hydroxide in water or milk of lime (calcium hydroxide suspended in water). Lime is only slightly soluble in water, 70 grains reckoned as quicklime, dissolving in a gallon of water at the ordinary temperature, $\frac{70}{70000} = \cdot 1$ per cent., so that the bulk of liquid required for softening is much greater when using lime water than milk of lime, as in the latter only a small part of the lime is dissolved, and most of it is suspended in the liquid. The makers of plant, using lime water, claim that the definite solubility of lime in water is a natural factor which should be made the most of in working a softening plant, and that by measuring the quantity of saturated lime water they have a means of accurately and automatically regulating the quantity of lime that is added, so that neither an excess or a deficiency need occur. There is a good deal to be said for this point of view. The quantity of reagents added to soften water must be carefully regulated, or more harm than good may be done. The chemical reaction involved in the removal of temporary hardness is of a very simple character. The lime in the form of calcium hydroxide neutralises and combines with half the carbonic acid contained in the bicarbonates with the formation of a double precipitate of calcium carbonate :—

$CaH_2(CO_3)_2$	+	$Ca(OH)_2$	=	$2CaCO_3$	+	$2H_2O$
Calcium bicarbonate (soluble in water).		Lime water.		Calcium carbonate (insoluble in water).		Water.

The permanent hardness, which is due mostly to sulphate of calcium, is not removed by the addition of lime, but requires carbonate of soda. The reaction is represented by the following equation :—

$CaSO_4$	+	Na_2CO_3	=	$CaCO_3$	+	Na_2SO_4
Calcium sulphate.		Sodium carbonate.		Calcium carbonate (insoluble in water).		Sodium sulphate (soluble in water).

Carbonate of soda is usually added in the form of soda ash, a water free substance which consequently goes further than the crystalline forms (see Table VI.). In some cases, where the water is rich in bicarbonates or contains much free carbonic acid, caustic soda may be advantageously employed.

Both soda ash and caustic soda are readily soluble in water, differing in this respect from lime, so that there is no difficulty in preparing a solution of any required strength for addition to the water (for strengths and sp. gr. of solutions see Tables XVII. and XVIII.).

These reactions require a short time to complete themselves, and in any softening plant it is necessary to provide tanks of sufficient size for the reactions to take place and the precipitated carbonate to deposit. In some plants, partly in order to minimise the size of the reaction tanks, a tank is provided for holding part or whole of the precipitate; but in any case it is essential to provide tanks of sufficient size whatever method be chosen to remove the precipitate. This point is at times lost sight of, and I was on one occasion called in to examine and report on the action of a softening plant where no reaction tanks had been provided, and the mixture of lime milk and soda ash was merely pumped into the tubes which carried the supply direct to the filter. Needless to say, the arrangement was wholly inadequate, and the softening process took place to a large extent in a tank intended for holding the softened and filtered water, the bottom of which was soon covered with a deposit of calcium carbonate.

When first formed the calcium carbonate precipitate is in a very finely divided state, so that it is by no means easily removed by filtration. The filter soon begins to clog, so that in all plant where filters are used some means must be provided either for the automatic cleansing of the filter or for the easy removal of the filtering medium and replacement by fresh.

The reactions involved in the process of water softening, especially those in removing permanent hardness, take place more readily when the liquid is warmed, and some softening plants are so arranged that the waste steam from the engine is conducted into the softening tank, thereby heating the water to be softened and completing the reaction. In this manner softening plant and condenser are combined in one, as the feed-water is heated and softened at the same time.

The quantities of reagents required for softening water are based on the equations already given, but are not really so easily calculated as might appear. In the first place, magnesium salts do not always behave in the same way as calcium salts. Bicarbonates of magnesium are precipitated by lime, but the action may proceed further, part of the magnesium bicarbonate being precipitated as hydroxide. Further, lime also acts on magnesium sulphate, producing magnesium hydroxide and calcium sulphate, as follows:—

$$MgSO_4 + Ca(OH)_2 = Mg(OH)_2 + CaSO_4.$$

From the point of view of scale formation, calcium sulphate is more objectionable than magnesium sulphate. Again, many waters contain free carbonic acid, which must be allowed for in calculating the quantity of reagents. In general it may be said that the principle to be followed for waters containing both temporary and permanent hardness consists in the addition of sufficient soda to decompose all sulphates of lime and magnesia together with enough lime to absorb all the carbonic acid left over by the soda reactions.

These calculations should be checked by laboratory experiments, in which a definite quantity of water, such as a liter, is softened with carefully-measured quantities of the reagents; the flask is corked and the precipitate is allowed to settle, after which quantities of 50 c.c. are decanted or filtered off for testing.

The Permutit Water-Softening Process.—During the last few years a novel method of water softening has been introduced which is based on the reactivity of *Permutit*, an artificial zeolite, a sodium aluminium silicate. This material in a granular condition is packed into towers through which the water to be softened is allowed to percolate. The calcium and magnesium salts in the water react with the permutit, the sodium content of which is gradually replaced by the calcium and magnesium which are therefore rendered insoluble and are retained by the mass of permutit as calcium and magnesium aluminium silicates. The equivalent of sodium thus displaced from the permutit dissolves in the water under treatment and is therefore contained in the purified water chiefly as sodium bicarbonate. The process therefore differs from the ordinary lime soda processes, in that the temporary hardness is not removed but replaced by sodium bicarbonate. This, however, for many industrial purposes, *e.g.* soap works, laundries, etc., is no drawback. After a time, owing to accumulation of lime and magnesia in the permutit, the latter ceases to be effective; the material is then regenerated by allowing a 9 per cent. solution of common salt to percolate through it. The salt reacts with the calcium and magnesium aluminium silicates, reforming the sodium aluminium silicate, while calcium and magnesium chloride pass into solution. The salt solution must be used in excess, only about 10 per cent. of it reacting, so that the issuing liquor contains about 8 per cent. of salt and 1 per cent. of the chlorides of calcium and magnesium. The water purification proceeds in the cold and is stated to be complete. The loss in permutit is said to amount to only 5 per cent. per annum.

Various objections have been raised to the use of this process for purifying water for steam raising. It is obvious that the carbonate of soda will accumulate in the boiler, and, if it does not act on the boiler plate, it may dissolve old deposits which have formed between the plates so that the boiler begins to leak. It will also attack most of the brass fittings and packings and may also cause priming. In any case it is necessary to blow down frequently to get rid of the accumulated salt, which means a loss of steam and heat. The process is also said to be unsuitable for waters containing free carbonic acid, iron, alkaline chlorides or solid particles. For certain purposes it would appear to have great advantages in the paper mill. In some cases, where a very hard water has to be treated, it is preferable to first remove the greater part of the temporary hardness with lime, and subsequently to soften fully with a permutit treatment. When considering the action of permutit in removing *permanent* hardness, it must not be forgotten that the ordinary treatment of the water with caustic soda results in the treated water containing an amount of sodium carbonate equivalent to the sulphates removed, so that, as regards permanent hardness and the accumulation of sodium carbonate, the permutit process and the caustic soda process are on a par.

Water-Softening Plants.—These are mechanical contrivances utilising the chemical reactions which have been explained above. Considerable ingenuity has been exercised to measure out automatically the lime and other ingredients in the right proportion, to distribute these evenly throughout the water under treatment, and finally to clarify the water after treatment and to remove the finely divided precipitates of the carbonate and sulphate of lime.

Seeing that the concentration of a saturated solution of lime in water is not much influenced by the temperature, a clear saturated solution of lime may be employed and the amount adjusted to the flow of the water to be treated. A form of stirrer or other contrivance is required to ensure a thorough mixture of the steam of lime water with that of the water to be treated. In the place of lime water we may use milk of lime, that is lime suspended in water, but in that case a definite quantity of lime must be added to a definite quantity of water in a tank provided with an efficient stirrer. Similarly, carbonate of soda or caustic soda solutions, if employed, must be prepared of a definite concentration. The addition of these ingredients to the water in definite proportions may be effected by means of oscillating receivers, that is, buckets hinged to a horizontal shaft and balanced by a weighted lever As soon as the bucket has received a certain weight of liquor, it tips up and delivers this into the reservoir. Or tanks provided with syphons may be employed which automatically discharge the liquor through the syphon tube when the tank is filled to a definite height. Or the proportions of the softening liquor may be adjusted by suitable valves.

The reaction chambers where the softening actually takes place are frequently fed at the bottom so that the softening takes place as the liquid mixture slowly rises in the chamber. These chambers are usually made cylindrical or conical and provided with baffle plates which help the precipitate to collect and fall. In some plants the reaction mixture is heated by steam as the reaction proceeds more quickly at a higher temperature. The heat is not wasted if the water is used straight away as feed water for the boiler. It has been found that the precipitate formed settles more readily if mixed up with the precipitate from a previous treatment. This principle is made use of by allowing the precipitate in the reacting tank to accumulate when it grows denser and the particles increase in size. The process makes use of the well-known fact that the particles of a precipitate tend to increase in size owing to the gradual dissolution of the smallest particles, resulting in the deposition of additional matter on the larger particles, which consequently grow at the expense of the smaller ones. The treatment of the water in this case is not continuous but intermittent, and after the tank has been filled up with the correct proportions of water and softening ingredients air is blown through by means of perforated pipes for ten minutes or so, by which means the precipitate from the previous operation which has become granular or flocculent is distributed through the reacting liquor and carries down with it the freshly formed, finely divided precipitate. It will be readily understood that the relatively large particles of the previous precipitate will settle more rapidly and carry down with them the freshly formed precipitate which is much more finely divided.

The removal of the precipitate formed in the process of softening is perhaps the most difficult problem and is the point of first importance in the construction of the plant. Many water-softening plants remove only part of the precipitate by sedimentation, and resort is had to a filter to remove the residue. These filters are usually of sand or wood wool. The sand filters can be made automatic, that is to say, when they begin to clog, the sand is stirred up by a current of water or air in the reverse direction by which the surface layer of material which causes the clogging is broken up. With wood wool filters it is necessary to repair the filtering medium from time to time.

These short descriptions will give some idea of the ingenious automatic appliances for softening and filtering water. For purposes of clarification where oily matter is present, as in condensed water, or water containing organic matter, the reagent mostly employed is alumino-ferric or some other crude sulphate of alumina. It is added direct to the water in conjunction with lime or soda, where oily condensed water has to be clarified. Special plants for treating oily water are supplied by makers of water-softening plant.

CHAPTER V.

RAW MATERIALS AND DETECTION OF ADULTERANTS.

An account will be given of the analysis and valuation of the more important chemicals used in the manufacture of paper and pulp.

Lime or quicklime is the oxide of the metal calcium (CaO) obtained by heating limestone (a form of calcium carbonate) in kilns, until the whole of the carbonic acid is driven off as carbon dioxide gas (lime burning). If the heating is not sufficiently intense or prolonged to drive off all the carbon dioxide, some calcium carbonate remains behind with the lime and must be reckoned as an impurity. Such lime after slaking effervesces when moistened with dilute hydrochloric acid. Lime which has been exposed to a moist atmosphere will also contain some carbonate through absorption of carbon dioxide gas from the atmosphere.

Provided the lime has been properly burnt and stored, its purity will depend upon the original limestone from which it was made. Most limestones contain some quantity of silica and silicates in the form of clay, flint, sand, etc., which of course find their way into the lime in a somewhat altered condition. Such lime has frequently greater cementitious value than the purer varieties or fat limes, and is largely used by the building trade, but for papermaking, the chemical and allied industries, the purer the lime the better. Perhaps the best limestone for making pure lime is found in the neighbourhood of Buxton, and some of it shows on analysis 2 per cent. or even less impurities. Limes of this type are known as "stone limes." The poorer qualities containing silicates, termed grey lime or shell lime, may not contain more than 50 or 60 per cent. of pure calcium oxide. Whatever lime the papermaker uses, the only substance it contains of value to him is the calcium oxide, whether it be used for water-softening, rag-boiling or any other purposes. The prices should be compared on the basis of the percentage of CaO the sample contains, and even then preference should be given to the purer limes as the silicious ones do not slake so readily and yield a larger percentage of sludge, the removal of which entails labour. Dirty limes should be rejected. Compact stones yield a smaller volume of sludge, and are therefore more economical.

Lime combines with water to form slaked lime or calcium hydroxide ($Ca(OH)_2$), one part of lime requiring about one-third its weight of water. This enters into chemical combination with the lime, so that pure calcium hydroxide or slaked lime is a dry substance and contains no water. In practical work it is usual to add a much larger quantity than this. A rough idea of the purity of a sample of quicklime may be obtained by noting the manner in which it slakes. Place a small lump the size of a walnut in a basin, and pour a small quantity of water upon it. A good sample of fat lime immediately absorbs the water and swells up with the development of much heat, so that part of the water passes off as steam, the swollen lump falling to a powder. With inferior silicious limes, change in temperature is hardly noticeable, and the lump hardly swells at all, and takes much longer to slake. On stirring up slaked lime with more water a turbid liquid is obtained known as milk of lime. In this form it is frequently used. Slaked lime and water are put into a tank with an agitator ; solid gritty particles and other impurities settle to the bottom and the milk of lime is drawn off.

The amount of lime in milk of lime may be roughly estimated by means of a hydrometer. Table XVI. gives in parallel columns the degrees Tw., grams (CaO) per liter, equivalent to lbs. per 100 gallons for a fat lime.

TABLE XVI.

MILK OF LIME.

SPECIFIC GRAVITY EXPRESSED IN DEGREES TWADDELL COMPARED WITH LBS. PER 100 GALLONS.

Degrees Twaddell.	Lbs. per 100 Gallons or Grams CaO per Liter.
2	11·7
4	24·4
6	37·1
8	49·8
10	62·5
12	75·2
14	87·9
16	100
18	113
20	126
22	138
24	152
26	164
28	177
30	190
32	203
34	216
36	229
38	242
40	255
42	268
44	281
46	294
48	307
50	321

To dissolve lime completely a very large quantity of water is necessary, 70 grains (CaO) requiring a gallon of water at the ordinary temperature (60° F. or 15° C.). This is equivalent to a solubility of ·1 per cent. or 1 gram to the liter.

Analysis—Free Calcium Oxide (CaO).—The estimation of the actual amount of calcium oxide in a sample of quicklime presents some difficulty. The correct method is as follows :—

Having procured an average sample, 100 grams are weighed out and carefully slaked in a mortar. The mass is then ground in successive quantities of cold recently-boiled distilled water, and the whole washed into a half-liter flask with the aid of a wash bottle and a funnel in the mouth of the flask. The liquid is made up to the mark and the flask corked and thoroughly shaken. Before any of the lime has had time to settle, 50 c.c. of the milk of lime are removed with a pipette and run into a second 500 c.c. flask. This second flask is then made up to the mark again with cold recently-boiled distilled water and 50 c.c. removed as before with a pipette. These 50 c.c. will be equivalent to 1 gram of lime, and represent the amount used for the test. It is titrated in a flask with normal oxalic acid (63 grams crystalline acid per liter). A few drops phenol-phthalein solution are added to the liquid as an indicator. This in the presence of caustic lime develops a red colour, which is destroyed, the liquid becoming colourless as soon as sufficient oxalic acid has been added to combine with all the free lime present. If the lime contains no carbonate or only traces, normal hydrochloric acid can be used instead of oxalic acid, but if calcium carbonate be present, oxalic acid is necessary, as hydrochloric acid would attack and dissolve the calcium carbonate before the indicator changed colour. Each c.c. normal acid is equivalent to ·028 gram calcium oxide (CaO) or ·037 gram calcium hydroxide ($Ca(OH)_2$). In other words, the percentage of calcium oxide (CaO) is obtained by multiplying the number of c.c. normal acid required by 2·8, or, if required in terms of calcium hydroxide, by multiplying by 3·7.

Calcium Carbonate ($CaCO_3$).—By modifying the process for estimating calcium oxide just described, the calcium carbonate may be estimated. One titration is carried out with oxalic acid as before. A fresh portion of the milk of lime is then taken, equivalent to 1 gram of lime, and titrated with normal hydrochloric acid, using methyl orange as an indicator. This will give the number of c.c. normal acid required to neutralise both the calcium oxide and calcium carbonate present in the sample. The difference between this and the number of c.c. required when titrating with oxalic acid gives the number of c.c. required to neutralise the carbonate alone. One c.c. normal acid is equivalent to ·05 gram $CaCO_3$.

I append analyses of three samples of lime together with the number of yards per ton (Beadle) :—

Description.	Quicklime (CaO).	Chalk ($CaCO_3$).	Yds. per Ton.
(1). Buxton lime . . .	95·2	4·1	1·54
(2) A hard lime . . .	88·9	10·5	1·78
(3) Otford lime . . .	80·2	16·7	2·5

I have already explained that the value of any lime will depend on the percentage of calcium oxide (CaO) it contains. Further, it should be noted that very frequently the higher the percentage of calcium oxide the heavier the lime, and therefore the fewer the yards per ton. These facts should be taken into consideration where lime is sold by the yard. Suppose that the prices of (1) and (3) are 17s. and 18s. per ton respectively, the corresponding prices per yard being

$$(1)\ \frac{17}{1{\cdot}54} = 11\text{s. } 4\tfrac{1}{2}\text{d., and } (3)\ \frac{18}{2{\cdot}5} = 7\text{s. } 2\text{d.}$$

In order to determine the relative values of (1) and (3), it is merely necessary to work out the price per ton of actual quicklime (calcium oxide) thus :—

$$(1)\ \frac{17 \times 100}{95} = 17\text{s. } 9\text{d. per ton CaO.}$$

$$(3)\ \frac{18 \times 100}{80} = 22\text{s. } 6\text{d.} \quad ,, \quad ,,$$

No. 3 is therefore actually some one and a quarter times dearer than No. 1, although the price per yard gives the reverse impression, namely, that No. 1 is half as dear again as No. 3.

Moisture and Carbon Dioxide.—About 1 gram of the sample of lime is weighed into a platinum crucible and strongly ignited in a blow-pipe flame for ten minutes or a quarter of an hour ; the loss in weight will give the amount of moisture and carbon dioxide driven off. Ignition for five minutes at a time must be continued until no further loss in weight takes place.

Sand and Silicious Matter.—If a sample of the lime be slaked and treated with an excess of dilute hydrochloric acid, all lime and calcium carbonate will be dissolved, leaving as an insoluble residue most of the sand or silicious matter it contains. Ten grams may be taken, and after treatment with acid washed free from any acid on a filter paper, ignited in a crucible and weighed. This will give some idea of the percentage of grit and sludge which will deposit on slaking the lime in the preparation of milk of lime. To estimate more accurately the proportion of sand and silica, a weighed quantity is treated with hydrochloric acid as before in a porcelain dish, and the contents evaporated to dryness and heated for half an hour in an air bath at 150° C., in order to render all the silica insoluble. On cooling, the contents of the dish are moistened with strong hydrochloric acid and transferred to a filter paper with a jet of hot water and thoroughly washed till free from acid. The residue is ignited in a crucible and weighed as before.

Sodium Carbonate or Soda.—This substance finds extensive use in the paper-making industries, generally in conjunction with lime for rag-boiling, water-softening, etc. The lime reacts with sodium carbonate in solution to form sodium hydroxide or caustic soda, and calcium carbonate, so that for rag-boiling a similar effect may be got by adding caustic soda straight away as is sometimes done.

Two forms of sodium carbonate are met with in commerce :—

(1) Crystallised sodium carbonate $Na_2CO_3\ 10H_2O$ (27·1 per cent. NA_2CO_3 or 21·7 per cent. Na_2O). This is commonly known as soda crystals or washing soda ; the white crystals effloresce when exposed to the air, that is, they lose part of their water, crumbling to a white powder.

(2) Soda ash or refined alkali Na_2CO_3 (58·4 per cent. Na_2O). This is the water-free salt, and is in consequence a more concentrated form than the preceding. It is prepared by two processes : the Leblanc soda, which varies considerably in purity (75 to 98 per cent. Na_2CO_3), and the ammonia or Solvay soda, which is a uniformly purer product containing 96 to 98 per cent. Na_2CO_3, but more bulky than the Leblanc soda and, therefore, more expensive to transport.

Analysis.—This resolves itself into a determination of the percentage of pure alkali, generally reckoned as Na_2O. It is effected by titration with standard acid. One c.c. of normal acid is equivalent to ·031 gram Na_2O. Weigh out 10 grams of the sample, dissolve in 100 c.c. distilled water and mix thoroughly. Wash out a 10 c.c.

pipette with a little of the liquid, then take 10 c.c. (= 1 gram) for titration with normal acid, and add a few drops of methyl orange solution. Normal sulphuric or hydrochloric acid is then run in from a burette—at first quickly and then a few drops at a time—until the yellow colour *begins* to take a reddish hue, showing that the whole of the alkali is neutralised. The number of c.c. required represents the percentage Na_2O contained in the sample.

The titration should be repeated with a fresh 10 c.c. of liquor, and the results should not differ by more than one-tenth of a c.c. The number of c.c. required multiplied by 3·1 gives the percentage alkali (Na_2O), or multiplied by 5·3 gives the percentage soda (Na_2CO_3) contained in the sample.

Some confusion is likely to arise as to the percentage of alkali in soda, which may be reckoned either as Na_2O or Na_2CO_3. As pure Na_2CO_3 contains 58·4 per cent. Na_2O, a sample of soda ash containing, say, 98 per cent. Na_2CO_3, will show on analysis only $98 \times \frac{58{\cdot}4}{100} = 57{\cdot}2$ p.c. (approx.) Na_2O.

Soda crystals are usually very pure and should not contain more than traces of sodium chloride and sulphate.

The accompanying table gives the percentage of Na_2O and Na_2CO_3 in solutions of different concentration, as measured by the hydrometer.

TABLE XVII.

Specific Gravities of Solutions of Sodium Carbonate. 60° F. = 15° C. (based on Lunge).

Degrees Twaddell.	Percentage by Weight.		Pounds per 10 Gallons or Percentage by Volume.	
	Na_2O.	Na_2CO_3	Na_2O.	Na_2CO_3.
1	0·28	0·47	·27	·47
2	0·56	0·95	·56	·95
3	0·84	1·42	·84	1·43
4	1·11	1·90	1·13	1·93
5	1·39	2·38	1·42	2·43
6	1·67	2·85	1·71	2·92
7	1·95	3·33	2·01	3·43
8	2·22	3·80	2·30	3·94
9	2·50	4·28	2·60	4·46
10	2·78	4·76	2·96	4·98
11	3·06	5·23	3·21	5·50

TABLE XVII. *(continued)*.

Degrees Twaddell.	Percentage by Weight.		Pounds per 10 Gallons or Percentage by Volume.	
	Na_2O.	Na_2CO_3	Na_2O.	Na_2CO_3.
12	3·34	5·71	3·52	6·03
13	3·61	6·17	3·83	6·55
14	3·88	6·64	4·14	7·08
15	4·16	7·10	4·45	7·61
16	4·42	7·57	4·76	8·15
17	4·70	8·04	5·08	8·70
18	4·97	8·51	5·41	9·25
19	5·24	8·97	5·73	9·80
20	5·52	9·43	6·05	10·34
21	5·79	9·90	6·38	10·91
22	6·06	10·37	6·71	11·48
23	6·33	10·83	7·04	12·04
24	6·61	11·30	7·38	12·62
25	6·88	11·76	7·72	13·19
26	7·15	12·23	8·06	13·78
27	7·42	12·70	8·40	14·38
28	7·70	13·16	8·74	14·96
29	7·97	13·63	9·10	15·56
30	8·24	14·09	9·45	16·10

CAUSTIC SODA, SODIUM HYDROXIDE, OR CAUSTIC ALKALI.—This substance, formula $NaOH$ (77·5 per cent. Na_2O), is usually sold in air-tight, iron drums, and forms a hard white mass, containing varying quantities of sodium carbonate, sulphate, water and other impurities, and quoted from 50 to 77 per cent. Na_2O. It rapidly absorbs both moisture and carbon dioxide from the atmosphere, and samples, if kept, should therefore be preserved in well-closed vessels.

The samples for analysis are taken from the freshly-opened drum when the caustic is broken up for dissolving. In this way samples can be taken from several drums, as they are opened from time to time, and stored in a large well-stoppered bottle. The pieces should not be larger than filberts. When representative samples have been collected from a sufficient number of drums the whole is well mixed. About 100 grams are weighed off into an already counterpoised porcelain dish. The weight need not be correct to less than a decigram. Nothing is gained by weighing off an exact number of grams, as the operation takes too long and absorption of moisture is going on all the time. With a little practice somewhere about

100 grams can be quickly weighed off and dissolved in about 200 c.c. of warm distilled water. The solution is then poured into a liter flask, cooled and made up to 1000 c.c.; 10 c.c. are taken for analysis and titrated with normal acid after diluting with recently boiled distilled water, using methyl orange as an indicator, as in the valuation of soda ash. One c.c. normal acid is equivalent to ·031 gram Na_2O or ·04 gram NaOH. Taking an example: 105·4 grams were dissolved in 1000 c.c. of water, the quantity taken for titration was therefore 1·054 grams. To calculate the percentage Na_2O divide the number of c.c. acid required by 1·054 and multiply by 3·1. If the result is required in terms of NaOH, multiply instead by 4·0. In commerce it is usually expressed in terms of Na_2O.

It is obvious that in the above analysis any sodium carbonate will be reckoned as caustic, as both neutralise the normal acid. Any considerable proportion of carbonate may be detected by adding acid, when effervescence will be noticed. The actual estimation of small quantities of carbonate in the presence of caustic alkali can be effected by a slight modification of the titration with acid. A few drops of a solution of phenol-phthalein are added to the liquor, well diluted with recently boiled and cooled distilled water, in the place of methyl orange, and the acid run in until the red coloration originally developed is just destroyed and the number of c.c. required noted. The acid should be run in, allowing the tip of the burette to touch the side of the dish or flask—I prefer a flask—and mixing the contents by a gentle whirling motion so as to disturb the liquid as little as possible. Shaking tends to cause loss of carbon dioxide gas, and impairs the accuracy of the test. A few drops of methyl orange are added, and the addition of acid from the burette continued until the yellow colour begins to turn pink. The burette is then read again.

With titrations of this sort the end point of the reaction may be passed over in the first titration, but having found the approximate number of c.c. required, another titration is made, adding straight away rather less than before, and determining the end point by adding the acid a drop at a time, carefully mixing between each addition and noting any change of colour. Where phenol-phthalein is used as an indicator, the pink colour is destroyed at the moment when the whole of caustic alkali and half the alkaline carbonate are neutralised, that is to say, when any carbonate is converted into bicarbonate. On adding methyl orange the colour does not change until the whole of both caustic and carbonate are completely neutralised. The difference between the figures obtained with the two indicators will therefore represent half the carbonate. On doubling this figure the number of c.c. N acid required to neutralise the alkaline carbonate is obtained, and subtracting this from the total number of c.c. required with methyl orange as an indicator, we shall have the number of c.c. required to neutralise the caustic alkali alone. In commerce the percentage Na_2O, present as caustic soda, calculated on the total Na_2O, is termed the percentage causticity.

To take an example: 10 c.c. of the alkaline liquor (containing 1·04 of substance) required 23·3 c.c. normal acid to destroy the red colour with phenol-phthalein, and a further addition of ·4 c.c. to develop a reddish shade with methyl orange. The total alkali as Na_2O was therefore $23{\cdot}7 \times 3{\cdot}1 \times \frac{1}{1{\cdot}04} = 70{\cdot}5$ per cent.

Further, of the total of $23{\cdot}3 + {\cdot}4 = 23{\cdot}7$ c.c. acid required, twice the difference between the two titrations, equal to ·8 c.c., represents carbonate, and therefore of the total 23·7, ·8 c.c. less, or 22·9 c.c., were required to neutralise the caustic soda. The percentage causticity is therefore $\frac{22{\cdot}9}{23{\cdot}7} \times 100 = 96{\cdot}6$ per cent.

A table is given showing the specific gravity of caustic soda solutions with the corresponding percentage of Na_2O and $NaOH$.

TABLE XVIII.

Specific Gravities of Solutions of Caustic Soda (60° F. or 15° C.) (based on Lunge).

Twaddell.	Pounds per 10 Gallons or per cent. by Volume.		Twaddell.	Pounds per 10 Gallons or per cent. by Volume.	
	Na_2O.	NaOH.		Na_2O.	NaOH.
1	·37	·48	31	12·32	15·90
2	·75	·97	32	12·77	16·48
3	1·13	1·46	33	13·22	17·06
4	1·51	1·95	34	13·68	17·65
5	1·88	2·42	35	14·13	18·23
6	2·26	2·92	36	14·58	18·81
7	2·64	3·41	37	15·04	19·41
8	3·02	3·90	38	15·49	19·99
9	3·39	4·38	39	15·94	20·57
10	3·77	4·86	40	16·40	21·16
11	4·16	5·37	41	16·94	21·86
12	4·55	5·87	42	17·47	22·54
13	4·94	6·37	43	18·01	23·24
14	5·32	6·86	44	18·55	23·94
15	5·71	7·37	45	19·09	24·63
16	6·10	7·87	46	19·63	25·33
17	6·49	8·37	47	20·17	26·03
18	6·88	8·88	48	20·70	26·71
19	7·27	9·38	49	21·24	27·41
20	7·65	9·87	50	21·78	28·10
21	8·04	10·37	51	22·34	28·82
22	8·43	10·88	52	22·89	29·54
23	8·82	11·38	53	23·44	30·25
24	9·21	11·88	54	24·00	30·97
25	9·60	12·39	55	24·55	31·68
26	10·05	12·97	56	25·10	32·39
27	10·50	13·55	57	25·66	33·11
28	10·96	14·14	58	26·21	33·82
29	11·41	14·72	59	26·76	34·53
30	11·86	15·30	60	27·32	35·25

TABLE XVIII. (*continued*).

Twaddell.	Pounds per 10 Gallons or per cent. by Volume.		Twaddell.	Pounds per 10 Gallons or per cent. by Volume.	
	Na_2O.	NaOH.		Na_2O.	NaOH.
61	27·93	36·04	81	40·52	52·28
62	28·54	36·83	82	41·18	53·14
63	29·15	37·61	83	41·84	53·99
64	29·77	38·41	84	42·50	54·84
65	30·38	39·20	85	43·16	55·69
66	30·99	39·99	86	43·82	56·54
67	31·60	40·77	87	44·48	57·39
68	32·22	41·57	88	45·14	58·25
69	32·83	42·36	89	45·80	59·10
70	33·44	43·15	90	46·46	59·95
71	34·08	43·97	91	47·23	60·94
72	34·72	44·80	92	47·99	61·92
73	35·36	45·63	93	48·76	62·92
74	36·01	46·46	94	49·53	63·91
75	36·65	47·29	95	50·29	64·89
76	37·29	48·12	96	51·06	65·88
77	37·93	48·94	97	51·82	66·86
78	38·57	49·77	98	52·59	67·86
79	39·21	50·59	99	53·36	68·85
80	39·85	51·42	100	54·12	69·83

MINERAL ACIDS — SULPHURIC AND HYDROCHLORIC ACIDS.—Both sulphuric and hydrochloric acids are occasionally required in the mill. Strong sulphuric acid or oil of vitriol is a heavy oily liquid, sp. gr. 1·85. The commercial acid contains various impurities including lead and arsenic; the lead if present in quantity is easily detected by diluting the acid when it separates out as a fine white precipitate, giving the liquid a milky appearance. This precipitate settles on standing, and the diluted acid, almost free from lead, may be poured off. Various acids of different purity and strength are sold, including the brown chamber acid, sp. gr. 1·6, and the concentrated brown oil of vitriol, sp. gr. 1·7. Great care is necessary in handling strong acid owing to its corrosive properties, and when required dilute should be poured in a thin stream into water, stirring all the while, as much heat is developed and there is danger of the acid spirting.

Analysis.—Dilute about 10 grams with water, and make up to 100 c.c., and take 10 c.c. for titration with normal alkali (caustic or carbonate), using methyl orange as an indicator. The alkali is added until the solution is yellow, showing no trace of red colour.

$$\frac{\text{c.c. N alkali reqd.} \times \cdot 049 \times 100}{\text{weight of acid taken}} = \text{the percentage strength}$$

of the acid in question. The acid may also be estimated by precipitation with barium chloride solution, as in the case of soluble sulphates (see alum, p. 89).

TABLE XIX.

SULPHURIC ACID.

SPECIFIC GRAVITY OF SULPHURIC ACID EXPRESSED IN DEGREES TWADDELL COMPARED WITH THE PERCENTAGE COMPOSITION AND POUNDS PER GALLON (LUNGE AND ISLEN).

Tw.	100 Pts. by Weight contain		Lbs. per Gallon.	Tw.	100 Pts. by Weight contain		Lbs. per Gallon.
	SO_3.	H_2SO_4.			SO_3.	H_2SO_4.	
40	22·30	27·32	3·28	65	34·35	42·08	5·57
41	22·82	27·95	3·37	66	34·80	42·66	5·67
42	23·33	28·58	3·46	67	35·27	43·20	5·77
43	23·84	29·21	3·55	68	35·71	43·74	5·86
44	24·36	29·84	3·64	69	36·14	44·28	5·96
45	24·88	30·48	3·73	70	36·58	44·82	6·05
46	25·39	31·11	3·82	71	37·02	45·35	6·14
47	25·88	31·70	3·91	72	37·45	45·88	6·24
48	26·35	32·28	4·00	73	37·89	46·41	6·33
49	26·83	32·86	4·09	74	38·32	46·94	6·43
50	27·29	33·43	4·18	75	38·75	47·47	6·53
51	27·76	34·00	4·26	76	39·18	48·00	6·62
52	28·22	34·57	4·35	77	39·62	48·53	6·72
53	28·69	35·14	4·44	78	40·05	49·06	6·82
54	29·15	35·71	4·54	79	40·48	49·59	6·92
55	29·62	36·29	4·62	80	40·91	50·11	7·02
56	30·10	36·87	4·72	81	41·33	50·63	7·11
57	30·57	37·45	4·81	82	41·76	51·15	7·21
58	31·04	38·03	4·90	83	42·17	51·66	7·30
59	31·52	38·61	5·00	84	42·57	52·15	7·40
60	31·99	39·19	5·10	85	42·96	52·63	7·50
61	32·46	39·77	5·19	86	43·36	53·11	7·59
62	32·94	40·35	5·29	87	43·75	53·59	7·69
63	33·41	40·93	5·38	88	44·14	54·07	7·79
64	33·88	41·50	5·48	89	44·53	54·55	7·89

TABLE XIX. (*continued*).

Tw.	100 Pts. by Weight contain		Lbs. per Gallon.	Tw.	100 Pts. by Weight contain		Lbs. per Gallon.
	SO_3.	H_2SO_4.			SO_3.	H_2SO_4.	
90	44·92	55·03	7·98	126	58·09	71·16	11·60
91	45·31	55·50	8·08	127	58·43	71·57	11·70
92	45·69	55·97	8·17	128	58·77	71·99	11·81
93	46·07	56·43	8·27	129	59·10	72·40	11·92
94	46·45	56·90	8·37	130	59·45	72·87	12·02
95	46·83	57·37	8·46	131	59·78	73·23	12·12
96	47·21	57·83	8·56	132	60·11	73·64	12·22
97	47·57	58·82	8·66	133	60·46	74·07	12·33
98	47·95	58·74	8·76	134	60·82	74·51	12·44
90	48·34	59·22	8·86	135	61·20	74·97	12·56
100	48·73	59·70	8·96	136	61·57	75·42	12·67
101	49·12	60·18	9·06	137	61·93	75·86	12·78
102	49·51	60·65	9·16	138	62·29	76·30	12·89
103	49·89	61·12	9·26	139	62·64	76·73	13·01
104	50·28	61·59	9·36	140	63·00	77·17	13·12
105	50·66	62·06	9·46	141	63·35	77·60	13·23
106	51·04	62·53	9·57	142	63·70	78·04	13·34
107	51·43	63·00	9·67	143	64·07	78·48	13·46
108	51·78	63·43	9·77	144	64·43	78·92	13·57
109	52·12	63·85	9·87	145	64·78	79·36	13·69
110	52·46	64·26	9·96	146	65·14	79·80	13·81
111	52·79	64·67	10·06	147	65·50	80·24	13·92
112	53·12	65·08	10·15	148	65·86	80·68	14·04
113	53·46	65·49	10·25	149	66·22	81·12	14·16
114	53·80	65·90	10·35	150	66·58	81·56	14·27
115	54·13	66·30	10·44	151	66·94	82·00	14·39
116	54·46	66·71	10·54	152	67·30	82·44	14·51
117	54·80	67·13	10·64	153	67·65	82·88	14·63
118	55·18	67·59	10·75	154	68·02	83·32	14·75
119	55·55	68·05	10·85	155	68·49	83·90	14·89
120	55·93	68·51	10·96	156	68·98	84·50	15·04
121	56·30	68·97	11·07	157	69·47	85·10	15·19
122	56·68	69·43	11·18	158	69·96	85·70	15·34
123	57·05	69·89	11·28	159	70·45	86·30	15·49
124	57·40	70·32	11·39	160	70·94	86·90	15·64
125	57·75	70·74	11·50				

Hydrochloric acid is sold as a solution of the gas in water containing about 30 to 36 per cent. of the dissolved gas. The chief impurity is iron, which imparts a yellow colour to the strong acid. The strength of the acid is estimated by titration with normal alkali exactly as in the case of sulphuric acid.

$\frac{\text{c.c. N alkali reqd.} \times \cdot 0365 \times 100}{\text{weight of acid taken}}$ = percentage strength of the acid in question. The iron is estimated colorimetrically, as described under water, the acid being diluted to a convenient strength according to the amount of iron it contains.

TABLE XX.

HYDROCHLORIC ACID.

SPECIFIC GRAVITY OF HYDROCHLORIC ACID EXPRESSED IN DEGREES TWADDELL COMPARED WITH THE PERCENTAGE COMPOSITION AND POUNDS PER 10 GALLONS (LUNGE AND MARCHLEWSKI).

Tw.	100 Pts. by Weight contain HCl.	Lbs. per 10 Gallons or Grams per 100 c.c.	Tw.	100 Pts. by Weight contain HCl.	Lbs. per 10 Gallons or Grams per 100 c.c.
0	0·16	·16	21	20·97	23·2
1	1·15	1·2	22	21·92	24·3
2	2·14	2·2	23	22·86	25·5
3	3·12	3·2	24	23·82	26·7
4	4·13	4·2	25	24·78	27·8
5	5·15	5·3	26	25·75	29·1
6	6·15	6·4	27	26·70	30·3
7	7·15	7·4	28	27·66	31·5
8	8·16	8·5	29	28·61	32·8
9	9·16	9·6	30	29·57	34·0
10	10·17	10·7	31	30·55	35·3
11	11·18	11·8	32	31·52	36·6
12	12·19	12·9	33	32·49	37·9
13	13·19	14·1	34	33·46	39·2
14	14·17	15·2	35	34·42	40·4
15	15·16	16·3	36	35·39	41·8
16	16·15	17·4	37	36·31	43·0
17	17·13	18·6	38	37·23	44·3
18	18·11	19·7	39	38·16	45·6
19	19·06	20·9	40	39·11	46·9
20	20·01	22·0			

Bleaching Powder or Chloride of Lime.—This substance is prepared by absorbing chlorine gas in slaked lime, and is manufactured in enormous quantities for bleaching purposes. There is a limit to the amount of gas absorbed by the lime, some of which remains apparently unchanged even in the strongest bleaching powder. In the freshly-prepared state, when fully charged with chlorine, bleaching powder may be represented by the formula $2CaOCl_2, Ca(OH)_2$, which corresponds to about 40 per cent. active or "available chlorine," but it is seldom if ever met with in commerce yielding more than 39 per cent. available chlorine, while 36 per cent. may be taken as the average for a good sample, and 35 per cent. is almost universally the guaranteed minimum. It may be preserved without much loss of activity if stored in a cool, dry place out of contact with the air, but gradually loses chlorine. The bleach liquor prepared from the powder is, as might be expected, less stable, but, according to Beadle,[1] it may be stored in tanks without appreciable loss of chlorine for six weeks except in hot weather.

Analysis. — It may be necessary to determine the strength both of the powder and of the liquor, for which purpose it is necessary to determine the amount of available chlorine ; that is, the chlorine which is capable of exerting an oxidising action and in virtue of which the bleaching effect is produced. Bleaching powder or the liquor may also contain chlorine in the form of calcium chloride which has no bleaching action and which is therefore not available.

For rough purposes *where the quality of the bleach is known* the following table may be applied for determining the strength of the bleach liquor.

---

[1] *Chapters on Papermaking*, vol. i., p. 40.

TABLE XXI.

SPECIFIC GRAVITY OF BLEACH LIQUOR IN TERMS OF DEGREES TWADDELL COMPARED WITH ITS STRENGTH EXPRESSED AS LBS. OF 35 °/₀ BLEACHING POWDER PER 10 GALLONS AND AVAILABLE CHLORINE IN GRAMS PER LITER (BASED ON LUNGE AND BACHOFEU).

Degrees Twaddell.	Dry 35 °/₀ Bleaching Powder, lbs. per 10 Gallons, or percentage by Volume.	Available Chlorine Grams per Liter.
½	·40	1·40
1	·77	2·71
2	1·59	5·58
3	2·42	8·48
4	3·26	11·41
5	4·13	14·47
6	4·96	17·36
7	5·84	20·44
8	6·79	23·75
9	7·61	26·62
10	8·46	29·60
11	9·34	32·68
12	10·23	35·81
13	11·17	39·10
14	12·09	42·31
15	13·06	45·70
16	14·27	49·96
17	14·93	52·27
18	15·77	55·18
19	16·69	58·40
20	17·57	61·50
21	18·43	64·50
22	19·43	68·00
23	20·43	71·50

Determination of Available Chlorine.—There are two methods of determining the available chlorine in bleaching powder, which will be described. In either case the first operation is the preparation of a solution of the powder; in other words, a bleach liquor of definite strength. Ten grams of the powder are weighed out into a dish and transferred to a fair-sized mortar, and distilled water added, a few c.c. at a time. The mixture of water and powder are thoroughly rubbed into a paste, and the rubbing continued as further water is added until the whole is diluted to a thin cream. The solid matter is allowed to settle for a while, and the liquid is decanted into a liter flask; the residue in the mortar is again rubbed with more water, allowed to settle and the liquid poured off and the process repeated, until the whole of the solid has been transferred to the flask. The contents are then made up to the mark with water, thoroughly mixed and an aliquot portion withdrawn with a pipette for analysis, without allowing the sediment to settle. It is necessary to take the turbid liquid when analysing the dry powder to determine whether it comes up to guaranteed strength ; but the test will correspond better to the actual conditions under which bleach liquor is employed in the mill if the sediment be allowed to settle and some of the clear liquid withdrawn for analysis as the sediment always retains a little of the active chlorine. When testing bleach liquor the clear liquid is, of course, always taken.

Estimation by Means of Sodium Arsenite Solution.—A standard (decinormal) solution of sodium arsenite is prepared by dissolving 4·95 grams of arsenious oxide in a solution of sodium carbonate. The arsenious oxide is finely powdered, dried by standing over night in a desiccator and carefully weighed. It is then introduced into a flask of 200 or 300 c.c. capacity, with about 20 grams of pure sodium carbonate dissolved in 100 to 200 c.c. distilled water. The mixture is gently shaken and warmed on a water bath for some time until the arsenious oxide is completely dissolved. The mixture is then cooled and made up to 1 liter. As an indicator, starch iodide paper is required. To prepare this, a dilute starch liquor is made by mixing 1 part of starch into a cream with water, and pouring it slowly into about 100 times the quantity of distilled water previously heated to boiling. After the liquid has boiled gently for a minute or two, when care must be taken to see that it does not boil over, a small quantity, say, 1 part of potassium iodide, is added, previously dissolved in a little water. The liquid is mixed, allowed to stand to deposit any sediment, and strips of unsized paper soaked in the solution and hung up to dry, out of contact with disturbing influences and fumes.

By means of a pipette take 25 c.c. (equivalent to ·25 gram of bleaching powder) of the milky bleaching-powder liquor which should be freshly prepared ; allow to flow into a flask and titrate with standard arsenite solution from a burette. The arsenite solution is added in small quantities at a time, stirring continuously, and after each addition a drop of the liquid is applied to a piece of the starch iodide paper by means of the glass rod used for stirring. As long as any bleach is present in the solution, it will liberate iodine from the potassium iodide in the paper, which, acting on the starch, will produce a blue colour. The addition of sodium arsenite solution is, therefore, continued until a drop of the solution no longer produces a blue colour on the starch iodide paper. The volume of the liquid added from the burette is noted. One c.c. standard sodium arsenite solution is equivalent to ·00355 gram of available chlorine. To obtain, therefore, the percentage of available chlorine in the bleaching powder originally used, multiply the number of c.c. required by $(4 \times \cdot355) = 1\cdot42$.

Estimation by Titrating Iodine Liberated from Potassium Iodide with Sodium Thiosulphate.—Twenty-five c.c. of the turbid bleach liquor, prepared as before, is allowed to run into an excess of freshly-prepared potassium iodide solution. Each determination will require about half a gram of the iodide. The effect of the bleach liquor is to liberate iodine which dissolves in the excess of potassium iodide every atom of available chlorine liberating an atom of iodine.

A standard solution (decinormal) of sodium thiosulphate (often although incorrectly termed hyposulphite) is prepared by crushing sufficient crystals, pressing between blotting paper to absorb any fluid enclosed in the crystals and dissolving 24·83 grams in water and making up to a liter.

This decinormal thiosulphate is run from a burette into the potassium iodide solution containing the liberated iodine. The brown colour changes to yellow, and the addition of thiosulphate is continued until the last faint yellow colour is just discharged. The end point is more apparent if a little starch solution be added. This is prepared by boiling starch with at least a hundred times the quantity of water as already described, allowing the sediment to settle, and pouring off the clear liquid. One or two c.c. of this liquid is added just before the pale yellow colour is discharged. Thiosulphate is then cautiously added until the blue colour disappears.

The $\frac{N}{10}$ thiosulphate is equivalent to the $\frac{N}{10}$ arsenite used in the previous method of estimating available chlorine, so that the calculation is the same in both cases. While standard arsenic solution is fairly permanent and keeps unchanged for months; standard thiosulphate begins to lose strength in a few days. It is therefore advisible to make up the thiosulphate fresh when required, which is easily done, or to keep a standard solution of iodine to check the strength from time to time.

As a standard (decinormal) iodine solution is required for other purposes, it will be as well to describe its preparation here. For the present purpose 250 c.c. will be sufficient to prepare at a time. 3·18 grams are weighed on a counter-poised watch glass as rapidly as possible. Iodine is volatile even at the ordinary temperature of the air, so that it will slowly lose weight on the pan. The contents of the watch glass are tipped into a beaker and dissolved in a small quantity of water with the aid of about 5 grams of potassium iodide crystals. Gently stir the liquor and allow to stand until all the iodine appears to have dissolved, and thoroughly rinse the watch glass. Pour off slowly into a 250 c.c. flask. Any undissolved iodine will remain at the bottom of the beaker, and must be treated with a little more potassium iodide and water to dissolve it. Transfer the whole to the 250 c.c. flask as well as rinsings from the beaker, make up to the mark with distilled water and mix thoroughly. This procedure is preferable to putting the iodine direct into the measuring flask with potassium iodide and water, as it is then exceedingly difficult to see when all the iodine is dissolved. By dissolving in a beaker (or other convenient vessel) and decanting, any undissolved iodine cannot escape notice.

Twenty-five c.c. of the standard iodine are now titrated with the thiosulphate added from a burette, with a little starch solution as an indicator added near the end of the reaction. Exactly 25 c.c. of thiosulphate should be required—if more or less the figure should be noted on the label of the bottle together with the date when the test was made. The necessary correction can then be applied. Supposing 26·4 c.c. thiosulphate were required, all results got when using this thiosulphate must be multiplied by $\frac{25}{26{\cdot}4}$. This factor may be noted on the label. Or, if preferred, the thiosulphate solution may be diluted or strengthened until it is of exactly decinormal strength.

This method for estimating the available chlorine in bleach is more rapid than the first one described, where arsenite solution is used, but is liable to error if the bleach happens to contain chlorates. Another objection if numerous analyses have to be made is the high price of iodine and its preparations.

ANTICHLORS—SODIUM SULPHITE, BISULPHITE AND THIOSULPHATE.—These substances are added in small quantity to the beater after the bleaching process is complete, in order to destroy any residue of bleach liquor left in the pulp. Any such residue would have the effect of bleaching and decolorising a dye subsequently added, besides being a source of danger if left in the pulp both to the paper and fittings of the paper machine.

Sodium sulphite $Na_2SO_37H_2O$ and bisulphite $NaHSO_3$ are salts of sulphurous acid H_2SO_3; they reduce any residue of hypochlorite to chloride, and are themselves at the same time oxidised to salts of sulphuric acid or sulphates. Both sodium sulphite and bisulphite may be bought anhydrous in the form of powder and are readily dissolved in water; cold or only slightly warm water should be used. They should be stored in a dry place and the cover replaced over the cask after withdrawing the required quantity. If allowed to get moist, they rapidly oxidise in the air to the corresponding sulphates and are then useless.

The efficiency of these substances as antichlors depends entirely on the percentage sulphurous acid (SO_2) free or combined. This is best determined by adding a small quantity of the powdered crystals or liquor to an excess of $\frac{N}{10}$ iodine solution, and titrating back the excess of iodine with an $\frac{N}{10}$ solution of thiosulphate. The difference will give the amount of $\frac{N}{10}$ iodine reduced by the sulphurous acid in the sample. ·1 gram of the finely powdered sodium sulphite is weighed out and placed in a beaker or flask with 20 c.c. $\frac{N}{10}$ iodine, and gently agitated until the powder has dissolved and the reaction is complete. $\frac{N}{10}$ thiosulphate solution is then cautiously added till the yellow colour is destroyed; a little starch may be added to make the end point of the reaction more easily detected, especially if working by gas light, when the eye is less sensitive to yellow shades.

One c.c. $\frac{N}{10}$ iodine is equivalent to ·0032 gram SO_2. To determine the percentage SO_2, subtract the number of c.c. $\frac{N}{10}$ thiosulphate used from 20 and multiply by 3·2.

Sodium thiosulphate or "hyposulphite" $Na_2S_2O_35H_2O$ is also used as an antichlor. It is estimated by dissolving 10 grams in 100 c.c. distilled water, and titrating 10 c.c. of this solution with $\frac{N}{10}$ iodine. One c.c. $\frac{N}{10}$ iodine is equivalent to ·0248 gram sodium thiosulphate.

ALUM—POTASH ALUM, ALUMINIUM SULPHATE, ETC.—Under this heading I shall consider a group of substances commonly used in conjunction with rosin size for engine sizing, for addition to gelatine in tub-sizing, for mordanting fibres and other purposes.

True alum is a double salt of potassium (or ammonium) sulphate with aluminium sulphate containing 24 molecules of water.

Potash alum, K_2SO_4, $Al_2(SO_4)_3$, $24H_2O$, contains 36 per cent. aluminium sulphate ($Al_2(SO_4)_3$), 45·6 per cent. water, 10·8 per cent alumina (Al_2O_3) and 33·7 per cent. sulphuric acid (SO_3).

Ammonia alum $(NH_4)_2SO_4$, $Al_2(SO_4)_3$, $24H_2O$, contains 37·8 per cent. aluminium sulphate and 47·8 per cent. of water.

Nowadays the trade term alum is often applied, although erroneously, to anhydrous aluminium sulphate, $Al_2(SO_4)_3$, which contains theoretically 29·9 per cent. alumina (Al_2O_3) and 70·2 per cent. sulphuric acid (SO_3).

Potash and ammonia alum occur in well-formed crystals and are separated in this state from the aqueous mother liquors in the course of manufacture. This process of crystallisation is one of those best adapted for the purification of chemical substances, and these crystallised alums are usually supplied in a high state of purity, containing only traces of iron, free acid being absent. For this reason they were at one time universally employed by the paper and textile trades for sizing and other purposes, in spite of the fact that they contained almost half their weight of water and only some 36 or 37 per cent. of aluminium sulphate, the active ingredient. This is seen by a glance at the percentage composition of potash and ammonia alums given above. The first attempts of manufacturers to supply aluminium sulphate of sufficient purity for papermakers' use were not successful, but the difficulties were eventually overcome, and this substance may now be had practically free from iron and free acid. It has consequently displaced for the most part the crystallised potash and ammonia alums.

Aluminium sulphate is prepared by the action of sulphuric acid on china clay. On treating the product with water the aluminium sulphate is dissolved out, leaving a silicious residue.

Aluminium sulphate is sold in three grades. The best quality consists of a hard, white, semi-opaque mass, containing less than ·0025 per cent. iron, the second quality containing less than ·2 per cent., while the cheapest quality contains considerably more. Of course the grade chosen will depend on the type of paper for which it is required. The third quality is also employed for the purification of water and effluents, for which purpose it finds extensive use under the name of alumino-ferric or concentrated alum.[1] By heating china clay with sufficient acid to decompose half of it only, or even less, a mass is obtained, termed "alum cake," which is intended to serve both for precipitating size and to serve as loading in the cheaper class of papers, such as "news." The loading consists of the silicious residue and china clay unacted upon by the acid. In this form, however, the mineral matter has a tendency to form lumps.

As to iron in alum it is stated by one authority[2] that as much as ·15 per cent. does no damage to a good writing, but anything over ·3 per cent. can only be used for inferior qualities.

---

[1] Alumino-ferric is, however, very generally employed for sizing paper where colour is of secondary importance.

[2] *Papier Zeitung*, 1891, p. 2327.

TABLE XXII.

Specific Gravity of Solutions of Aluminium Sulphate (based on Larsson).

Sp. Gr. at 15° C.	Degrees Twaddell.	Contain in Lbs. per 10 Gallons or per Cent. by Volume.		
		Alumina (Al_2O_3).	Sulphuric Acid (SO_3).	Aluminium Sulphate $Al_2(SO_4)_3$.
1·005	1·0	0·14	0·33	0·47
1·010	2·0	0·28	0·65	0·93
1·016	3·2	0·42	0·98	1·40
1·021	4·2	0·56	1·31	1·87
1·026	5·2	0·70	1·63	2·33
1·031	6·2	0·84	1·96	2·80
1·036	7·2	0·98	2·28	3·26
1·040	8·0	1·12	2·61	3·73
1·045	9·0	1·26	2·94	4·20
1·050	10·0	1·40	3·26	4·66
1·055	11·0	1·54	3·59	5·13
1·059	11·8	1·68	3·91	5·59
1·064	12·8	1·82	4·24	6·06
1·068	13·6	1·96	4·57	6·53
1·073	14·6	2·10	4·89	6·99
1·078	15·6	2·24	5·22	7·46
1·082	16·4	2·38	5·55	7·93
1·087	17·4	2·58	5·87	8·45
1·092	18·4	2·66	6·20	8·86
1·096	19·2	2·80	6·52	9·32
1·101	20·2	2·94	6·85	9·79
1·105	21·0	3·08	7·18	10·26
1·110	22·0	3·22	7·50	10·72
1·114	22·8	3·36	7·83	11·19
1·119	23·8	3·50	8·16	11·66
1·123	24·6	3·64	8·48	12·12
1·128	25·6	3·78	8·81	12·59
1·132	26·4	3·92	9·13	13·05
1·137	27·4	4·06	9·46	13·52
1·141	28·2	4·20	9·79	13·99
1·145	29·0	4·34	10·11	14·45
1·150	30·0	4·48	10·44	14·92
1·154	30·8	4·64	10·76	15·40
1·159	31·8	4·76	11·09	15·85
1·163	32·6	4·90	11·42	16·32

TABLE XXII. (*continued*).

Sp. Gr. at 15° C.	Degrees Twaddell.	Contain in Lbs. per 10 Gallons or per Cent. by Volume.		
		Alumina (Al_2O_3).	Sulphuric Acid (SO_3).	Aluminium Sulphate $Al_2(SO_4)_3$.
1·168	33·6	5·04	11·74	16·78
1·172	34·4	5·18	12·07	17·25
1·176	35·2	5·32	12·40	17·72
1·181	36·2	5·46	12·72	18·18
1·185	37·0	5·60	13·05	18·65
1·190	38·0	5·74	13·38	19·12
1·194	38·8	5·88	13·70	19·58
1·198	39·6	6·02	14·03	20·05
1·203	40·6	6·16	14·35	20·51
1·207	41·4	6·30	14·68	20·98
1·211	42·2	6·44	15·01	21·45
1·215	43·0	6·58	15·33	21·91
1·220	44·0	6·72	15·66	22·38
1·224	44·8	6·86	15·99	22·85
1·228	45·6	7·00	16·31	23·31
1·232	46·4	7·14	16·64	23·78
1·236	47·2	7·28	16·96	24·24
1·240	48·0	7·42	17·29	24·71
1·244	48·8	7·56	17·62	25·18
1·248	49·6	7·70	17·94	25·64
1·252	50·4	7·84	18·27	26·11
1·256	51·2	7·98	18·59	26·57
1·261	52·2	8·12	18·92	27·04
1·265	53·0	8·26	19·25	27·51
1·269	53·8	8·40	19·57	27·97
1·273	54·6	8·54	19·90	28·44
1·277	55·4	8·68	20·23	28·91
1·281	56·2	8·82	20·55	29·37
1·285	57·0	8·96	20·88	29·84
1·289	57·8	9·10	21·20	30·30
1·293	58·6	9·24	21·53	30·77
1·297	59·4	9·38	21·86	31·24
1·301	60·2	9·52	22·18	31·70
1·305	61·0	9·66	22·51	32·17
1·309	61·8	9·80	22·84	32·64
1·312	62·4	9·94	23·16	33·10
1·316	63·2	10·08	23·49	33·57
1·320	64·0	10·22	23·81	34·03

TABLE XXII. (*continued*).

Sp. Gr. at 15° C.	Degrees Twaddell.	Contain in Lbs. per 10 Gallons or per Cent. by Volume.		
		Alumina (Al_2O_3).	Sulphuric Acid (SO_3).	Aluminium Sulphate $Al_2(SO_4)_3$.
1·324	64·8	10·36	24·14	34·50
1·328	65·6	10·50	24·47	34·97
1·331	66·2	10·64	24·79	35·43
1·335	67·0	10·78	25·12	35·90
1·339	67·8	10·92	25·45	36·37

Analysis.—This comprises the following determinations: insoluble matter, alumina, sulphuric acid, iron and free acid.

Determination of Insoluble Matter.—A fair sample of alum is broken into small pieces in a mortar, and 5 grams dissolved in 200 c.c. of water. A good grade of alum usually dissolves to an opalescent solution, leaving little or no solid residue, while on the other hand, alum cake will of course consist of 50 per cent. or more of insoluble matter. If there is any appreciable amount of insoluble residue it is filtered off, and the filtrate collected in a 500 c.c. flask. The residue and the filter paper is washed with water till free from alum, the washings being collected with the filtrate in the flask, the contents of which are now made up to 500 c.c. and set aside for the analysis of alumina, sulphuric acid, etc. The filter paper and residue are ignited in a platinum crucible and weighed. The weight gives the amount of insoluble matter which should be expressed as a percentage on the original quantity of alum taken.

Determination of Alumina.—The contents of the 500 c.c. flask containing the soluble matter are thoroughly mixed, and 50 c.c. (equivalent to ½ gram of alum) withdrawn with a pipette and transferred to a beaker. The solution is diluted to about 100 c.c. with ammonium chloride solution, and weak ammonia *cautiously* added until the liquid smells distinctly but not strongly of the gas. It is then heated and the liquid kept boiling for a minute or two. Only a faint odour of ammonia should be apparent after boiling, but it is not advisable to drive off every trace of ammonia, as the precipitate is then very difficult to filter; on the other hand, precipitated alumina is distinctly soluble in ammonia, so that care must be taken that only a very slight excess remains in the liquid. The precipitated alumina is now filtered off, and any adhering to the sides of the beaker removed by means of a glass rod with a short piece of rubber tubing attached to the end. The sides of the beaker should be rubbed down with this rubber-tipped rod, and the loosened precipitate transferred to the filter with a jet of hot water from a wash bottle. The precipitate is thoroughly washed with hot water until the filtrate no longer contains sulphuric acid. This may be tested for by collecting a little of the filtrate in a test tube, acidifying with hydrochloric acid and warming with a little barium chloride solution. If sulphuric acid is still present, a precipitate or opalescence due to barium sulphate will be produced. When the precipitate is washed free of soluble salts the moist filter paper is transferred bodily to a platinum crucible, which is ignited and weighed, the weight of alumina being calculated as a percentage on the amount of alum originally taken, which in this case will merely mean multiplication by 200. The ignited alumina should be dead white in colour; any shade of yellow or red is an indication of the presence of iron.

Determination of Sulphuric Acid. — Another 50 c.c. (equivalent to ½ gram of alum) are taken for the estimation of sulphuric acid. As before, the 50 c.c. are transferred to a beaker, diluted with water, 10 c.c. of strong hydrochloric acid added and heated to boiling. The flame is then removed, and a strong solution of barium chloride cautiously added in excess; 5 to 10 c.c. will probably be sufficient. The liquid is then again heated for five or ten minutes and set aside for the precipitate of barium sulphate to settle. Another drop or two of barium chloride is then added to the clear liquid to make certain that an excess has been added. Should a precipitate result, more barium chloride must be added and the liquid heated to boiling again for a short while; the beaker is then set aside for the barium sulphate to settle, if possible allowing it to stand over night and the clear supernatant liquid poured through a filter paper without disturbing the precipitate more than is necessary. Hot water is now added to the precipitate, which is allowed to settle again, and the liquid poured off through the filter paper. In this manner the precipitate is washed two or three times by decantation, and is finally transferred to the filter paper with the aid of a jet of hot water from the wash bottle. Any precipitate adhering to the sides of the beaker is removed by means of the rubber-tipped rod and washed into the filter paper, but this should not be necessary. The precipitate is then washed repeatedly with hot water until free from chloride. This may be tested for by taking a small quantity of the filtrate in a test tube as before and adding a drop of silver nitrate solution, which should not produce any precipitate or opalescence ; the moist filter paper is transferred to a crucible, and ignited as in the case of the alumina. The weight found must be multiplied by the proper factor in order to obtain the amount of sulphuric acid, as described in Chapter II. The figure thus obtained, multiplied by 200 and the factor 0·343 (=68·6), will give the percentage sulphuric acid (SO_3).

Determination of Soluble Iron.—This estimation is carried out by a method similar to that described in Chapter IV. for the determination of iron in water, with the aid of the standard iron solution containing ·01 per cent. of iron in the ferric state. Fifty c.c. of the solution of alum are poured into a Nessler glass with two or three drops of nitric acid free from iron. One c.c. of a weak, freshly prepared solution of potassium ferrocyanide is added. If the quantity of iron present is very small, only a faint blue tint will be produced, but if the percentage of iron is larger the colour will be deeper. As it is not easy to compare the tints when the colour is very intense, if necessary a smaller quantity of the alum solution must be taken, say 25 or 10 c.c., and diluted up to the 50 c.c. mark on the Nessler glass with water. The colour developed is matched by producing a tint of the same depth in another glass by means of a standard iron solution containing an equivalent quantity of iron-free alum exactly as described in the estimation of iron in water. Alum is added to the standard, as its presence somewhat modifies the blue tint developed. The percentage of iron is calculated in the manner already described for water.

Determination of Free Acid.—As manufactured nowadays, it is unusual to find anything but traces of free acid in the better qualities of aluminium sulphate. Where free acid is present in only small quantities the determination is by no means an easy one. Some idea as to the probability of an excess of acid may be got by comparing the ratio of the percentages of alumina and sulphuric acid. For every molecule of alumina, $Al_2O_3 = 102$, there should be theoretically 3 molecules of sulphuric acid, $3SO_3 = 240$. But, as it is possible to have a basic aluminium sulphate, that is to say, an aluminium sulphate containing more alumina than is represented by the above ratio and yet to have free acid present, the latter must be tested for specially. The method usually adopted for detecting and measuring free acid depends on the solubility of free sulphuric acid in alcohol, aluminium sulphate being insoluble. Twenty grams of alum (aluminium sulphate) are finely powdered and dried at 100° for an hour or so and then placed in a dry flask with 50 c.c. absolute alcohol. The flask is well corked and set aside a few hours to stand. The alcohol is then filtered off and the residue treated with 20 c.c. fresh alcohol, which is poured through the same filter paper and the two alcoholic filtrates united. A large excess of water is now added, preferably after first distilling off most of the alcohol, and the solution titrated with decinormal caustic soda, using methyl orange as an indicator. From the number of c.c. caustic soda required, the percentage free sulphuric acid may be calculated. It is advisable where strict accuracy is required to make a blank test, using 70 c.c. alcohol, as the latter has not always a neutral reaction. If any flocculent white precipitate is seen floating in the liquid, it should be acidified with a few drops of hydrochloric acid and then made just alkaline with ammonia, the alumina filtered off and estimated in the usual manner. The quantity of sulphuric acid corresponding to that of alumina must now be calculated by multiplying the weight of alumina found by the factor $\frac{240}{102}$. This gives the amount of sulphuric acid (SO_3) which must be deducted from that found by titration in order to ascertain the total amount of free acid. In many samples of the good grades of alum which I have tested for free acid from time to time, the acid reaction of the alcoholic extract has been largely or wholly accounted for by the presence of the dissolved aluminium salt. Such samples may be safely passed as containing no free acid.

In addition to the systematic analysis of alum, it is also advisable to ascertain its size precipitating value, that is to say, the quantity of rosin size precipitated by a given amount of the alum under examination. For this purpose Griffin & Little's sizing test may be applied. A standard neutral rosin size solution is first prepared by dissolving about 25 grams of good ordinary rosin size in about 250 c.c. rectified spirit. The solution is filtered into a liter measuring flask to remove insoluble matter, and the contents of the flask diluted with a mixture of 500 c.c. rectified spirit and 300 c.c. of water; a few drops of phenol-phthalein solution are added, and then standard caustic soda solution, drop by drop, shaking after each addition until a faint permanent pink colour is produced. The contents of the flask are now made up to the mark with water, and thoroughly mixed.

The solution so produced is a standard solution of neutral sodium resinate; if it is not clear it should be set aside to stand, and the clear liquor filtered from the sediment. The value of the standard size solution is next determined by precipitating with a solution of pure crystallised ammonia alum, 5 grams of which are crushed and pressed between blotting paper and then dissolved in water and made up to 500 c.c. One c.c. of this solution will contain 0·1 gram of alum. To determine the value of the ammonia alum solution as against standard size solution, 20 c.c. of the latter are allowed to run into a flask of about 150 to 200 c.c. capacity two-thirds full of distilled water. The alum solution is now added from a burette a few drops at a time. Between each addition the flask is corked or closed with the thumb, vigorously shaken and set aside to stand until the flocculent precipitate has risen to the surface. The addition of alum is continued until the precipitate on rising leaves the solution entirely clear without any trace of milkiness or opalescence.

The amount of ammonia alum required to precipitate the 20 c.c. of standard size is obtained by multiplying the number of c.c. alum solution required by 0·1. If calculated on the weights of alum and neutral rosin size, it has been found that one part of ammonia alum precipitates 2·46 parts of size, so that it is only necessary to multiply the weight of ammonia alum found necessary to precipitate 20 c.c. size solution by the factor 2·46 to obtain the weight of size in 20 c.c. of the standard solution.

To find the precipitating value of any particular sample of alum a solution is prepared, as before, by dissolving 5 grams of the sample in 500 c.c., and filtering the solution, if necessary, through a dry filter paper. Twenty c.c. of the standard size solution are taken and titrated, as before, with the solution of alum. This gives the alum required to precipitate 20 c.c. of standard size. The weight of size in this 20 c.c. of standard size solution has already been determined by titration with standard ammonia alum, so that the amount of the sample of alum under investigation required to precipitate one part of the size is easily calculated.

ROSIN AND ROSIN SIZE.—Rosin or colophony is the residue left on heating the crude turpentine or pine rosin in a retort until all the moisture and turpentine are driven off. It forms a yellow to dark brown, brittle, transparent mass, according to the method of heating and temperature employed. Rosin used for size-making is almost entirely of American origin, the various qualities being distinguished by the letters of the alphabet; the darkest is marked "A," the brands becoming paler and less coloured as the letters ascend the alphabet. The palest and most transparent are distinguished by the letters "W." or "W.G." (water-glass), or "W.W." (water-white).

When broken, rosin shows a conchoidal (shell like) fracture; the broken surface should have a pure glassy appearance. A dull surface or one deficient in gloss may be due to presence of gum resins or similar bodies which dissolve in the alkaline liquids used in preparing size, and separate out again on cooling.

Attempts have been made to utilise the so-called rubber resins for the manufacture of size. This resin results from the extraction of Jelutong or Pontianac. It is friable but not properly saponifiable. It can be used to replace part of the free resin in the size, but even then the product is said to possess disadvantages over size prepared exclusively from colophony.

For examination of colophony, a representative sample, amounting to a few pounds, must be taken with due care from different portions of the bulk. This is reduced in quantity by crushing, halving and dividing as explained under sampling coal (p. 35), until only a few grains of finely powdered substance remain.

Determination of Insoluble Residue and Mineral Impurities.—Twenty grams are weighed out and dissolved in a small quantity of spirit, and the quantity of residue that remains undissolved is noted. If the amount is appreciable the alcoholic liquid is filtered off and the residue transferred to a filter paper, washed with a little more spirit until free from rosin, and then dried and weighed in a stoppered weighing bottle. The filter paper is of course previously dried and weighed in the bottle, and its weight is deducted from that of the paper with the residue, the difference giving the total insoluble residue. The filter paper and residue are now ignited in a platinum crucible, and the ash weighed. This will give the weight of the mineral impurities. The quantity found should not exceed 1 or 2 per cent.

Determination of Unsaponifiable Matter.—Rosin belongs to a class of chemical substances known as organic acids, and like all such bodies reacts with alkalies to form salts. When heated with caustic soda or sodium carbonate it forms a sodium salt, the rosin soap or size for sizing paper. Rosin usually contains some substances which are not capable of forming salts or soaps, these substances are classed together as unsaponifiable matter; the quantity found in American rosins does not usually exceed 10 per cent. The following table gives the percentages of unsaponifiable matter in some samples examined by Evans and Black:—

TABLE XXIII.

Unsaponifiable Matter in Rosin.

	Unsaponifiable Matter per Cent.
American "W.W."	7·34
,, "W.G."	5·00
,, "N."	9·00
,, "N."	8·21
,, "M."	7·61

The determination of unsaponifiable matter depends upon the fact that while it is easily soluble in ether, rosin soap is insoluble. Ten grams of the rosin are placed in a flask with a solution prepared by dissolving 5 grams of pure caustic soda in a small quantity of water, and adding 50 c.c. of alcohol. The flask is connected with an inverted condenser and heated for an hour or so on a water bath, so that it just boils. The alcohol is now distilled off, and the residue of soap dissolved in 50 c.c. hot water and transferred to a separating funnel. The flask is rinsed out with a few c.c. of water, and the combined alkaline liquids extracted with 50 c.c. ether. The ether and aqueous liquors are thoroughly mixed and set aside for the ether to separate out. This may take some little time, and it is as well to leave it over night. In the morning the lower aqueous layer is run off as completely as possible, and the ether left in the separating funnel washed by adding 10 or 20 c.c. of water, shaking up and allowing the water to settle. The water is drawn off and the ether transferred to a weighed flask and distilled off. The residue remaining in the flask and consisting of the unsaponifiable matter is dried by leaving the flask for an hour in the air bath at 100° to 110°, and the flask and contents weighed. The flask is then put back in the air bath for half an hour and re-weighed to make certain that all the moisture is driven off. The unsaponifiable matter is calculated as a percentage on the weight of rosin originally taken.

The unsaponifiable matter in rosin is apt at times to prove a source of trouble to the papermaker, in some cases it separates from the cooling size in crusts which form on the sides of the vessel. These crusts readily crumble and become detached, eventually finding their way into the paper and giving rise to "rosin spots."

Having determined the mineral impurities and unsaponifiable matter, the remainder may be regarded as consisting of pure rosin. From this the amount of alkali required to convert the rosin to rosin size may be calculated. The combining weight of rosin is 346, so that every 100 parts of pure rosin requires $\frac{31}{346} \times 100 = 8{\cdot}96$ parts of alkali, reckoned as Na_2O, or $\frac{53}{346} \times 100 = 15{\cdot}32$ parts of Na_2CO_3 for conversion to rosin soap. The amount of pure rosin (abietic acid) in a sample may also be determined by titration with caustic alkali. Ten grams of rosin are dissolved in alcohol (methylated spirit made neutral to phenol-phthalein will serve), and a few drops of phenolphthalein solution added, decinormal caustic soda is then run in till a permanent red colour is produced. One c.c. decinormal alkali is equivalent to 0·0346 gram pure rosin (abietic acid). The alcohol used should be tested beforehand to see that it is of neutral reaction. The test is also a check on the purity of the rosin, as the larger the percentage of abietic acid the more caustic soda is required to neutralise it.

The next point is sometimes difficult to ascertain with a dark coloured sample. Schwalbe suggests in such cases the addition of *neutral* calcium chloride solution, which produces a flocculent precipitate of the resin. This is allowed to settle or filtered off and the clear liquor titrated.

If instead of neutralising an alcoholic solution of rosin with caustic alkali, a weighed quantity of rosin be boiled with an excess of aqueous alkali, neutralisation of the abietic acid with the formation of the sodium salt or rosin soap will also take place, but in addition the alkali will attack other substances present in small quantity in commercial rosin, with the result that altogether more alkali will be required than for neutralisation alone. The operation of boiling rosin with an alkaline liquor, known technically as a saponification process, resembles the actual process used in the manufacture of rosin size. The process is therefore carried out on a small scale to determine what percentage of the commercial rosin is capable of reacting with alkalies to form rosin soap or size. Five grams of powdered rosin are gently boiled in a large porcelain dish covered with a clock glass, with exactly 25 c.c. N caustic soda, for an hour or so. The contents of the dish are then taken up with about 50 c.c. neutralised methylated spirit, a few drops of methyl orange added to the liquid, and N hydrochloric acid run in from a burette until the liquid turns red. The number of c.c. acid required is subtracted from 25, and gives the number of c.c. N alkali required to saponify the 5 grams of rosin and convert it completely into size. If the liquids are rather darkly coloured, it is a good plan when titrating to pour off a small quantity into a test tube, and to add to this a drop or two more methyl-orange, any red colour developed is then easily seen, or to treat with neutral calcium chloride solution as already described.

The percentage of saponifiable matter in the rosin reckoned as abietic acid may be calculated by multiplying the number of c.c. N alkali required to saponify the 10 grams of rosin by 34·6. The figure so obtained generally averages about 10 per cent. more than that obtained by *neutralising* an alcoholic solution with caustic alkali. Of course in the actual manufacture of size less alkali is usually taken than is necessary to saponify the whole of the rosin in order to leave some of the latter in the free state. Sodium carbonate is generally used in the place of the caustic soda in the above tests. The reaction, however, does not proceed so rapidly, and requires more prolonged heating. Some of the darker grades of rosin yield just as good size as the better qualities, the only drawback being the darker colour of the size prepared from them. The colour is, however, largely separated in the liquor, which comes to the surface on cooling and can be skimmed off.

ROSIN SIZE.—In order to obtain a fair sample the size should be stirred up and a portion withdrawn and put at once into a stoppered bottle. A preliminary examination may be made by dissolving a little in warm distilled water, noting how it dissolves and whether the free rosin remains suspended when the size solution is allowed to stand over till the next day. After standing, the milk of rosin is poured off, and the nature of any deposit on the bottom of the vessel is noted. If the particles of rosin are suspended in a very finely divided state, there is hardly any deposit on standing, except for coarser impurities which may be present.

The precipitate produced by adding a dilute solution of alum to the well-diluted rosin milk is also noted; it should be fine and flocculent and should not deposit rapidly. These tests are of value in drawing a comparison between different samples of size, but the same strengths of the size and alum solutions should always be adhered to or the results will not be comparable.

The test may be carried a step further and a quantitative relation fixed for the precipitating value of a definite quantity of alum solution against different samples of size (see under ALUM).

The foregoing tests are of a practical nature and should be supplemented by a systematic analysis. This consists of the following determinations: moisture, free rosin, combined rosin and total alkali.

Determination of Moisture.—Two or three grams of size are accurately weighed out on a tared watch or clock glass, preferably not less than about 8 cm. in diameter. It is then dried in an oven, at a temperature not exceeding 110° C. After two hours it is removed from the oven and placed in a desiccator to cool. It is now weighed and returned to the oven for another half-hour; cooled, weighed again and the process repeated until it ceases to lose weight.

The loss of weight represents moisture and other volatile matter. It is calculated as a percentage on the original weight of size taken and usually designated as moisture.

This figure obviously includes not only loss of moisture but also loss of any other volatile ingredients present. It is, however, sufficiently accurate for the purpose, and the increase in weight from oxidation during drying tends to balance matters.

As already explained, rosin is the residue left in the retort when the crude turpentine is distilled with the object of obtaining "oil" or "spirits of turpentine." It is hardly to be expected that the whole of the more volatile products are completely removed in this process. The rosin retains a trace of the volatile "spirits of turpentine" which finds its way into the rosin size. The quantity will depend on the temperature at which the crude turpentine was distilled and the manner in which the size was prepared. I made some careful experiments with a sample of size of well-known make to ascertain whether the proportion of turpentine and volatile matter other than water contained in the size is sufficient to impair the accuracy of the ordinary method of estimating moisture by drying down on a watch glass as already described. The test as applied is an alternate method for estimating moisture. The water and turpentine driven off by heating the size are collected in a graduated glass vessel (a burette serves the purpose) and measured off separately. The illustration (fig. 14) explains the apparatus used. Thirty to fifty grams of size are introduced into the weighed flask (A), which is reweighed, giving the weight of the size by difference. The flask is heated in the air bath (B), which may be made of a tin canister covered with asbestos board, or coated with a thick layer of asbestos composition such as is sold for the purpose of lagging steam pipes, a similar piece of board with holes cut to receive the neck of the flask and the thermometer serves as a lid. The flask is fitted with a bored cork carrying a bent piece of quill tubing of rather large bore leading to the burette. As the latter is used for delivering and not measuring liquids, it is filled with water before starting the test and the water run out down to the 50 c.c. mark. The flask is now gently heated, water and turpentine distil over—the latter first—and are condensed in the quill tubing and collect in the burette. The temperature is gradually raised until water ceases to distil over. The volume of the water is now read off and also that of the thin layer of turpentine on the top. As an additional check the flask (A) is weighed again with its contents on cooling, the loss of course representing moisture and volatile matter. A sample treated in this way gave, as an average of four tests, 38·75 per cent. water collected, the loss of weight of the flask averaging 39·55 per cent. The turpentine collected averaged ·34 per cent. and the moisture determined by drying on a watch glass in the usual manner 39·50 per cent. The loss in weight from volatile matter other than water was, therefore, inappreciable in this sample.

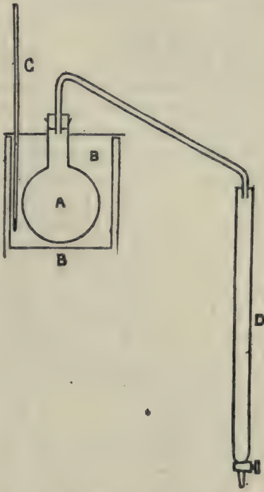


FIG. 14.—Direct Determination of Moisture in Rosin Size apart from other Volatile Bodies. A, Flask heated in Asbestos Air-bath B, Provided with Thermometer C; Water and other Volatile Substances collect in the Burette D, where the Volume is read off.

Determination of Free Rosin.—Three or four grams of size are accurately weighed off in a small beaker or evaporating dish and transferred to about 50 c.c. warm water in a separating funnel. A good plan is to weigh the dish containing size and a short glass rod all together. Some size is taken up on the end of the rod, as if it were treacle, and allowed to drop into the warm water in the separating funnel without wetting the rod or allowing it to touch the sides of the funnel. This is repeated two or three times until sufficient size has been allowed to drop into the funnel. The rod is then replaced in the dish, and the residue of size, dish and rod weighed together again. The difference between the two weights gives the weight of size taken for analysis. The separating funnel is now stoppered and the contents shaken until the size has dissolved to the usual milky liquor. Twenty c.c. of ether are added to the liquor and the whole cautiously but thoroughly mixed up. I prefer to use an ordinary cork in place of the usual ground-in glass stopper, as it is less likely to be blown out suddenly. Care should be taken in mixing up the aqueous and ethereal liquors that too high a pressure is not developed in the funnel. The two liquids are first gently mixed by turning the funnel upside once or twice, keeping a finger on the stopper, it is then held in an inverted position, cork downwards, and the stop-cock opened when air and ether vapour will escape with a rush. The cock is then closed and the mixing process repeated, inverting and opening the cock from time to time to release the pressure. *There is no need to shake vigorously,* as the liquids are thoroughly brought in contact by simply inverting a few times. Failure to bear this in mind has led some authorities to condemn the method of ether extraction as impracticable. Vigorous shaking tends to the formation of air bubbles, which hinder the ethereal layer from separating. This should be complete in ten minutes, when the separating funnel is set aside to stand. If the ethereal layer does not separate readily, a pinch of salt will often help matters. The under or aqueous layer is drawn off into a flask by opening the stop-cock, and should be removed as completely as possible without carrying any of the ethereal or upper layer with it. A few c.c. of water are now added to the ether remaining in the funnel, and the two are gently agitated together and the wash water drawn off. The ether, which now contains most of the free rosin in solution (the sodium resinate or rosin soap being insoluble in ether) is poured off through the mouth of the funnel into a small, tared flask. It is very easy to spill some of the ether in doing this, which, of course, spoils the whole analysis and makes it necessary to start afresh. The aqueous liquid and wash water are poured back into the funnel and a second extraction made with a fresh quantity of ether, as before. This will dissolve the greater part of any free rosin not removed in the first extraction. The aqueous liquors are carefully preserved for determination of combined rosin, while the ethereal extracts are united, the ether distilled off, and the residue of rosin dried in the air oven at 100° to 110° till it suffers no further loss in weight. The weight of free rosin is calculated as a percentage on the original weight of size. The apparatus for distilling off ether is shown in figure 15. The flask is heated in a water bath in which the water has already been heated to boiling and the flame turned out so as to run no risk of the ether catching fire. I should here emphasise the fact that ether vapour is very inflammable and no light should be left burning or brought near an open vessel containing ether. A flask containing ether should be only loosely stoppered if left on the bench, as should it get heated the pressure of vapour may burst a thin glass flask before it blows the cork out. The flask is attached to the condenser by a bent piece of glass-tubing, and at the further end of the condenser is placed a flask for collecting the ether that distils over. This may be returned to the stock bottle and used over again. If the condenser is of the Liebig type, as shown in figure 15, it should be a good long one. Cribb's condensers are effective and very compact.

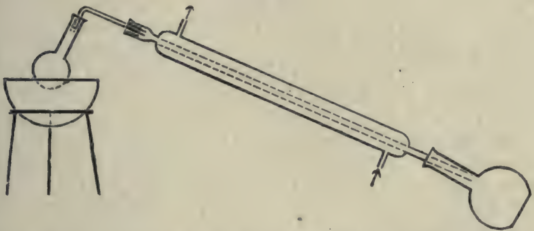


FIG. 15.—Apparatus for Distilling off Ether on a Water Bath.

Determination of Combined Rosin.—The aqueous liquors from which the free rosin has been extracted are returned to the separating funnel, and sufficient dilute sulphuric or hydrochloric acid added to decompose all the sodium resinate and liberate the combined rosin. A drop of methyl orange will show if sufficient excess of acid has been added. The separated rosin is extracted twice with ether in exactly the same manner as before, and the ethereal extracts united in a tared flask, the ether distilled off and the residue of rosin dried and weighed. As before, the combined rosin is expressed as a percentage on the weight of size originally taken. The total rosin is got by adding the percentages of free and combined.

Determination of Total Alkali.—A couple of grams of size are weighed out into a platinum crucible. The crucible and contents are cautiously heated to burn off the rosin, and the cinder strongly ignited until nothing but a white ash remains. This may be accelerated by allowing the crucible to cool from time to time and moistening the ash with a little ammonium nitrate solution and reheating. By this process all organic matter is burnt off, and the soda alone remains as sodium carbonate. The weight of the ash, therefore, gives the total alkali as sodium carbonate, from which the weight in the form of Na_2O is easily obtained by multiplying by the factor ·68. As an additional check the ash is dissolved out of the crucible by repeated treatments with hot water and titrated with $\frac{N}{10}$ acid, using methyl orange as an indicator. From the number of c.c. required, the amount of Na_2O is easily calculated as in the analysis of soda ash. If the figure for soda comes out lower by titration than by directly weighing the ash, it is due to a trace of mineral matter other than alkali in the original size. I append the complete analysis of a sample of size :—

Total rosin	56
Total soda (Na_2O)	3·6
Turpentine	0·3
Other Mineral Matter	0·2
Moisture	39·6
	99·7

Another method for analysing rosin size obviates the necessity of weighing the rosin by titrating it, using a factor for the equivalent of the alkali required. As I have already explained, 1 c.c. of decinormal alkali corresponds to ·0346 gram of pure rosin (abietic acid). For technical purposes the figure ·033 is sometimes employed. The procedure is as follows :—

A weighed sample of 2 or 3 grams is shaken up with warm water until completely emulsified ; 20 c.c. of $\frac{N}{10}$ sulphuric acid are then added, the liquid cooled and the total rosin extracted with ether in the same manner as for the free and combined rosin already described. The acid aqueous liquor is now titrated back to the neutral point by $\frac{N}{10}$ caustic alkali, using phenol-phthalein. The difference between the sulphuric acid used and the alkali required to neutralise, gives the sulphuric acid necessary to decompose the sodium resinate present in the size and liberate the combined rosin. The amount of combined rosin is calculated by means of the factor already given. The total rosin which has been extracted with ether is then titrated with an alcoholic solution of normal alkali, the total rosin being calculated from the number of c.c. required by the factor already referred to, in this case 0·33. By subtracting the figure for the combined rosin from the total rosin, the free rosin is obtained by difference. Any unsaponifiable matter in the total rosin can be determined at the same time by evaporation of the ethereal solution after neutralising as described. In this way the trouble of drying down and estimating the rosin direct is avoided. On the other hand, it is not so exact and the actual value of the factor used in the calculations varies with the source and quality of the rosin in the size. It has been stated that, in spite of this, the method is quite as exact because of the loss of volatile constituents when drying the rosin for the purpose of weighing it. The amount of loss, however, in such a case is very small. Thus, in three estimations of total rosin by extraction with ether, drying and weighing the rosin, I obtained the following figures: 55·8, 56·3 and 56·0, giving a mean figure of 56·0.

Schwalbe states that the titration method can be shortened by dissolving the rosin size in chloroform instead of emulsifying it with warm water. He states that all sizes will dissolve straight away in chloroform, water and the standard acid being subsequently added as described above. I have not, however, experienced any difficulty in getting 2 or 3 grams of size completely emulsified in warm water, and the use of chloroform presents doubtful advantages unless it is desired to use this solvent for extracting the rosin in preference to ether.

GLUE AND GELATINE.—A distinction is generally drawn between the two substances glue and gelatine for papermaking purposes. By glue the papermaker understands an adhesive material used to bind the mineral matter or coating to the body paper in the manufacture of coated or art papers, its suitability for this purpose depending chiefly upon its adhesive properties. By gelatine he understands a product used for sizing paper in the sheet or web; here the adhesive properties do not come into consideration, but rather those qualities of the gelatine which prevent the penetration of ink into the paper. As a matter of fact glue and gelatine are only different qualities of the same substance, gelatine being the more refined product. The raw material in both cases consists of hides and bones, the former being generally considered to yield a better product. The glue and gelatine are not contained as such in the raw material, but are produced on heating with water, in which they dissolve.

The purity of the product will, of course, depend largely upon the methods adopted for its manufacture. In the preparation of bone gelatine the mineral matter is dissolved out of the bone by means of hydrochloric or sulphurous acid, and the residual gelatinous mass extracted with water.

In the manufacture of glue it is usual to exhaust the bones without previous treatment with acid. When skins are used as raw material, the manufacture of glue and gelatine follows the same lines, the superior quality of the gelatine depending upon careful selection of the skins and greater care in preparation. Those mills which prepare their own gelatine for tub sizing, extract the skins and feet in copper cauldrons, skimming off the fat and running the clear liquor into pans to cool, the residue in the cauldrons being subjected to further extractions with hot water. The gelatinous liquid is mixed with a little alum solution to preserve it; the alum has also the effect of producing a stiffer jelly. In hot weather, when the jelly is very apt to decompose, a small addition of formaline is often made, which has a similar but more powerful action both as a preservative and for stiffening the jelly.

Analysis.—The analysis of glue and gelatine comprises the following determinations: (*a*) moisture, (*b*) ash, (*c*) water-absorbing power, (*d*) colour and opacity, (*e*) gelatinising power, (*f*) viscosity, (*g*) strength, (*h*) acidity, and (*i*) fatty matter.

Glue and gelatine are usually sold in sheet form. The sheets vary in thickness, the finer qualities of gelatine being usually supplied in the thinnest sheets. The thickness must be taken into consideration in forming an opinion of the colour and opacity of the glue by mere inspection of the sheets. Indeed it is hardly safe to come to a conclusion on this point without testing in the manner described below (*d*). Glue is often judged by the colour, smell and shrinkage, but such properties are not safe guides even with considerable experience. A good glue should, however, be well dried and almost free from smell. As to the gloss, this is liable to mislead, as glues with dull surfaces may be excellent adhesives.

(*a*) *Moisture.*—The amount of moisture contained in ordinary glue and gelatine varies considerably, but may be placed at 14 to 18 per cent. Too little moisture may point to over drying, which reduces the tenacity, while too much moisture may diminish the keeping qualities.

For the estimation, 2 or 3 grams are removed from the sheet by scraping with a coarse rasp and weighed in a tared watch glass. The watch glass and contents are dried for ten or twelve hours in the air oven at 100° to 110°, cooled in a desiccator and weighed. The loss in weight represents moisture. Care should be taken to treat all samples of glue for tests in the same manner, as many of the figures are of relative rather than absolute value. It is best to compare the samples under examination with one or two glues or gelatines of known qualities, whose properties and behaviour for the purpose required have been ascertained by experience in the mill.

(*b*) *Ash.*—Two grams are gently ignited in a platinum crucible until carbonised, the flame is then turned on full and the heating continued until the whole is burnt to a white ash. This is often a rather lengthy process. The crucible should be well inclined on its side in order to induce a draft of air, and may be allowed to cool from time to time, moistened with a little water or ammonium nitrate solution and re-ignited. In the course of manufacture substances such as sulphate and carbonate of lead, zinc oxide and salts of chromium and tungsten are added to the solution of glue before it sets to a jelly, with the object of improving the quality. Glues containing such substances yield, of course, a higher percentage of ash, and the adulterants may be identified by the ordinary tests. The examination of the ash will also in some cases afford evidence as to whether the raw material from which the glue was derived consisted of bones or hides. In the former case a fusible ash is obtained containing large quantities of phosphates, while the ash of hide glues does not fuse when the crucible containing it is heated in a Bunsen flame. The ash of hide glues has frequently an alkaline reaction derived from a residue of lime used in lining the skins and not completely removed by the subsequent acid treatment and washing.

(*c*) *Water-Absorbing Power.*—The object of this test is to determine how much water is absorbed when the glue or gelatine is immersed for twenty-four hours. For this purpose either a whole sheet or portion of a sheet in one piece is weighed off and immersed in cold water. The glue or gelatine gradually swells, absorbing water, and after twenty-four hours is taken out and weighed after any superfluous water has been drained off. The percentage weight of water absorbed is to some extent a measure of the quality of the material. Good qualities of glue will absorb eight or nine times their weight of water, but of course the amount will depend both on the thickness of the sheet and on the temperature of the water, so that experiments made, say, in summer and winter, are not directly comparable. There is also the liability of some glue going into solution, especially the lower grades, and in warm weather. To overcome the difficulties above referred to the temperature of the water may be kept constant, say, at 15° C.

(*d*) *Colour and Opacity.*—A portion of the glue which has been swollen with water in the last test may be conviently used for making a 5 per cent. solution. Glue and gelatine cannot be readily dissolved in warm water until they have first been allowed to swell by standing in cold water. To prepare a small quantity of solution rapidly, a little powder rasped off a sheet may be dissolved in hot water. The vessel in which the solution is prepared should be heated on a water bath and not directly by a flame. As soon as the glue is completely liquefied it is poured off and diluted to the required degree. Equal volumes of the 5 per cent. solution are poured into Nessler tubes, or test tubes selected so as to be of the same diameter and filled to the same height will do at a pinch. On cooling the solution will set to a jelly, and the colour and turbidity (opacity) of the samples may be compared. It is not necessary to fix a standard of colour, but the glues under investigation should be compared with some glue, the colour of which has been found satisfactory in practice. For the best tub-sized papers the colour of the gelatine cannot be neglected.

(*e*) *Gelatinising Power.*—This test is of considerable importance for judging the value of gelatine for sizing qualities. It is carried out by determining the strength of a jelly of definite concentration. Methods have been devised for testing the absolute weight required to break the surface of the jelly, but it is generally sufficient to compare 5 per cent. jellies made from different glues under the same conditions by merely feeling the stiffness of the jelly with the finger or thumb. The 5 per cent. solution as prepared above from the swollen gelatine may be used, the different samples being dissolved in a similar manner and avoiding prolonged heating on the water bath, as this tends to alter their qualities. The same quantity of the 5 per cent. solution of each sample is poured into dishes of the same size and allowed to set; the stiffness of the jelly is tested by pressing the surface with the finger or thumb. In this way it is quite easy to arrange them in order of superiority, that yielding the stiffest jelly heading the list. It will be found that in the case of several glues taken at random and treated in this manner, that two persons working independently usually class them in the same order of strength. The value of the gelatine under investigation may be judged from the position it takes up in order of strength as compared with those of known sizing qualities.

(*f*) *Viscosity.*—Here again the best means of judging a glue is to compare it with other glues of known qualities treated in the same manner, for this purpose the 5 per cent. solution should be diluted down to 1 per cent. and cooled to 15° Centigrade. The solution is then drawn up into a 50 c.c. pipette, and the time taken for the liquid to run out from the pipette is noted with a stop-watch. The longer the time taken the higher the viscosity and the better the quality of the glue or gelatine. In these tests care must be taken to always use the same pipette, as the time taken will depend upon the size of the orifice. At least a dozen tests should be made with each sample and the mean value taken.

(*g*) *Strength.*—It is sometimes of interest to know what effect sizing with gelatine will have on the strength and stretch of the paper. This may be arrived at by sizing sheets of water leaf with a solution of gelatine of the same strength and containing the same proportion of alum as is actually used in the mill. The sheets are first laid on the surface of the solution, and when the gelatine solution has penetrated to the upper surface the sheets are drawn through the liquor and squeezed by passing between a pair of rubber rolls and hung up to air dry. The weight of the sheets before and after sizing and air drying is noted, so that the percentage of gelatine taken up is in each case easily calculated. This is necessary, as with papers of varying substance the percentage of gelatine absorbed will not be the same. After hanging twenty-four hours to air dry, the sheets are cut up into strips and tested in a paper testing machine. In this way the actual quality of a sample of gelatine may be very thoroughly investigated, contrasting its effect on the paper with that produced by a sample of gelatine of known quality and sizing effect.

(*h*) *Acidity.*—Glues and gelatines sometimes contain mineral acids such as hydrochloric and sulphurous acids which have not been thoroughly removed in the course of manufacture; to estimate these 50 grams are allowed to swell in 80 c.c. of cold water in a flask. The flask is then connected with a condenser and heated in a water bath; a current of steam is introduced into the flask by another tube dipping below the surface of the liquid, and the water distilled over is collected until it amounts to about 200 c.c. The distillate is then titrated with decinormal caustic soda, using phenol-phthalein as an indicator. From the proportion of alkali required to neutralise the acid, the amount of the latter can be calculated. It should not exceed 2 per cent. on the weight of the glue or gelatine taken.

Fatty Matter.—If the fat is not completely removed from the bones used for the extraction of glue or gelatine, the latter may contain small quantities. To test for fats, 5 grams of glue are rasped or otherwise broken up and extracted with ether ; this may be done in a Soxhlet extraction apparatus (for description of Soxhlet, see p. 275, under the estimation of rosin in paper).

CASEIN.—Of recent years glue for coating paper has been replaced to a certain extent by casein, especially on the Continent of Europe and in the U.S.A. Enormous quantities of the watery liquid containing this substance in solution is left after the separation of fat from milk in the process of butter-making. The aqueous liquid is treated with acid or rennet, either of which has the effect of precipitating the casein ; in the former case the product is known as acid casein and the latter rennet casein. It is filtered off, washed free from acid and dried. Large amounts are produced in the United States and the Argentine Republic, but it is also made in quantity in various parts of the Continent. It comes into commerce as a sandy yellowish powder of varying degree of fineness. The more finely divided product is preferred as being easier to dissolve. When thoroughly dry, casein can be packed and stored in a dry room for an indefinite period without undergoing alteration, but the presence of even traces of moisture enables the micro-organisms to develop, bringing about putrefaction. It is therefore essential that the casein should be stored dry to prevent the decomposition. It is sprayed over with a small quantity of strong alcohol, 95 per cent., and packed immediately into cardboard boxes with a strip of paper pasted round the edges. Unlike glue, casein is insoluble in water and requires a mild alkaline substance to bring it into solution ; those usually employed are sodium carbonate, borax and ammonia.

Analysis.—Casein is liable to contain traces of the acid used in precipitating it and also of fat from the milk. It also contains a small quantity of water. The moisture is determined, as in the case of glue, by drying ; the fat by extraction with ether in a Soxhlet. The acid, if present, may be detected by shaking up the sample with distilled water, pouring off and testing for acid reaction with litmus paper. The acid may be identified, if necessary, in the usual manner ; hydrochloric, sulphuric, acetic and lactic acids are those most likely to be found.

STARCH.—Starch is added to the beater for the purpose of giving a certain feel to the paper. It has also a certain sizing effect.

The granules of which it is composed are very minute, and therefore the paper at times retains but a small proportion of what is added. Occasionally it is preferred to dissolve the starch previous to adding it to the beater. For this purpose it is made into a thin paste with *cold* water and the paste is poured in a thin stream into boiling water. The solution should not be boiled longer than necessary, as this tends to hydrolyse the starch. Starch varies somewhat in properties according to its origin, thus the granules of different starches vary in size. Each granule consists of a little sack containing glutinous starchy matter which swells when heated, so that on passing over the drying cylinders the sacks burst and the starchy matter finds its way between the fibres of the paper. The temperature at which the starchy cell or sack bursts is different for different starches, so that here again different sizing effects may be expected with starches of different origin.

Taking the commoner starches, the granules of potato starch are relatively large, those of maize smaller, while those of rice are smallest of all. Starches are readily identified by microscopic examination; figures (16-19) show drawings which I have made of some of the commoner starches. They are drawn as nearly to scale as possible so as to represent the relative magnitude of the starch granules. Their characteristics for purposes of identification may be shortly enumerated.

Potato (fig. 16).—Usually of oval form, about $\frac{1}{20}$ mm. long and $\frac{1}{37}$ mm. across, there is frequently a dark spot or hilum near the narrow end, and many of the cells have characteristic markings which, though faint, are quite distinct. A few of these are seen in the drawing.

Maize (fig. 17).—The granules are polygonal, though somewhat rounded in places, on an average $\frac{1}{70}$ mm. in diameter. Most of the granules show a distinct mark in the centre with radiate stellate lines.

Rice (fig. 18).—The granules are polygonal, like maize, but very much smaller.

Wheat (fig. 19).—The granules are circular, about $\frac{1}{60}$ mm. in diameter. A dark spot, but not usually in the centre, may be detected.

It must not be imagined that the granules of any particular starch are uniform in size. As will be seen from the drawings, they vary considerably and the figures for the diameter must be taken as somewhere about the average.


FIG. 16.—Potato Starch.

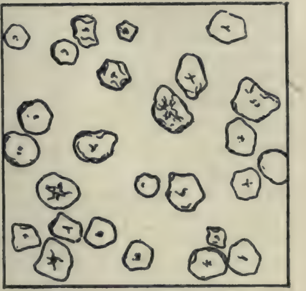


FIG. 17.—Maize Starch.

Analysis.—As regards the chemical analysis the most important determinations are those of moisture and mineral impurities, but some evidence as to the comparative value of the starches may also be obtained by making up starch jellies and comparing their strength, as described in the case of glue.

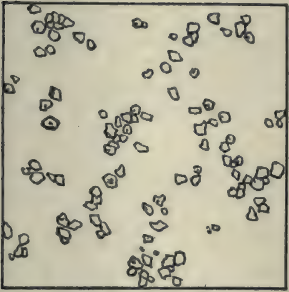


FIG. 18.—Rice Starch.

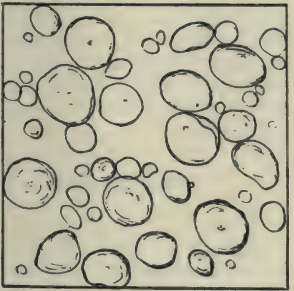


FIG. 19.—Wheat Starch.

Moisture.—Five grams of the sample are weighed out on to a tared clock-glass and dried in a water oven at 100° C. until the weight is constant; the loss of weight is reckoned as moisture. Starch will contain something like 10 or 15 per cent. under ordinary conditions; anything above 20 per cent. must be regarded as excessive and probably due to insufficient drying or to the starch having been stored in a damp place.

Mineral Matter.—For this purpose 2 grams are burned to ash in a platinum crucible; the residue should contain no traces of black carbonaceous matter; it may be necessary to allow the residue to cool and moisten with water, igniting again to burn completely to ash. The ash in starch does not generally exceed ½ to 1 per cent., anything over this will be due to added mineral matter, pointing to adulteration. If much mineral matter is found, a larger quantity of the starch should be ashed and the mineral matter subjected to an examination; probable adulterants are clay, chalk and gypsum. Even small quantities of mineral adulterants will be detected by examining the starch under the microscope, and the proportion can be roughly estimated from the appearance. Cases have also been recorded of adulteration of starch with cellulose in finely-divided form. On colouring the sample of starch with iodine and examining under the microscope, the particles of cellulose remain uncoloured or only slightly coloured, while the starch turns blue. Loaded starches are sometimes sold as such, but it is usually better for the papermaker to add pure starch and loading separately as he then knows exactly in what proportions he is adding them.

Minerals and Loading Materials.

China Clay or Kaolin.—Chemically this substance is a hydrated aluminium silicate. The composition varies somewhat, but clays usually contain 47 per cent. to 50 per cent. silica (SiO_2), 34 per cent. to 40 per cent. alumina (Al_2O_3), 12 per cent. to 15 per cent. water, and traces of iron, calcium, magnesium and alkali. The percentage of ferric oxide may approach to, but is usually considerably less than 1 per cent. in the best samples.

Its value as a filler or loading material depends upon the colour and absence of gritty or sandy particles. Its value for coating paper depends on the colour and the size of the particles (figs. 21-26) derived from the granite rocks from which the clay has been formed. In the course of manufacture the crude clay is stirred up with water and allowed to flow through a series of wooden troughs, arranged somewhat on the principle of a sand-table, where the coarser particles are deposited. The water carrying clay and mica next passes to a series of shallow troughs where most of the mica (fig. 24) is deposited, and from thence to a series of settling pits where the clay proper settles out. The finer the particles the further they will be carried before they are deposited, so that the best clay is deposited in the last pit.

Preliminary Examination.—The principle of separation by levigation may be made use of in examining a sample of clay. In the first place, a rough idea can be got by dropping a pinch into a tumbler of water, and noticing how the clay spreads in the water. The coarser particles fall straight to the bottom, while the finer particles remain suspended for a considerable time. Gritty particles may also be detected by spreading on a sheet of white paper with the blade of a knife or mixing a little of the clay with water and rubbing the paste with the finger, when it should give a smooth, even cream. If desired a test may be made to separate a sample of clay according to the size of the particles in a simple elutriating apparatus. This consists of a conical glass vessel, about 8 inches high, and provided with a smaller outlet tube near the top. A funnel with a long shank is loosely supported by a brass cap and dips to the bottom of the conical vessel. Ten or twenty grams of the clay are weighed out and placed in the vessel. A very slow current of water is then allowed to flow into the funnel from a water-tap, and, rising in the vessel, carries with it the finer particles of clay. After about ten or fifteen minutes the water will be tolerably clear, all the finer particles having been carried off, leaving only the coarser particles in the vessel. These are washed out into a tared dish or crucible, dried and weighed. The material may be separated into grades of different fineness by varying the rate at which the water is allowed to enter the funnel.

In comparing two samples of clay in this manner, it is necessary that the same conditions should be maintained in both cases, especially the pressure of water employed to wash the clay. The best arrangement is a large bottle on a shelf acting as reservoir, at a known height from the ground. The pressure of the water will be given by the difference in height between the outlet tube and the bottom of the tube A, as shown in the illustration (fig. 20).

A microscopic examination of a sample is also valuable in helping to form an opinion of the quality of the clay, especially as regards size of particles and the addition of ultramarine and other mineral blue (figs. 21-26). As to the colour of the clay, the whiter the better. Clays with a slight natural yellowish hue are sometimes artificially blued by the addition of ultramarine or a blue coal-tar dye. Such additions must be regarded as adulterants, as by this means clays of inferior colour are passed off as of best quality. It is much better for the papermaker when buying a cheaper clay to know what its natural colour is, and then add a little more blue in the beater, as may be required. Figs. 21 and 22 show a clay of very regular sized particles free from mica, while 25 shows one containing much mica. Fig. 24 shows the micaceous particles separated from the clay. Figs. 23 and 26 show other samples of clay.

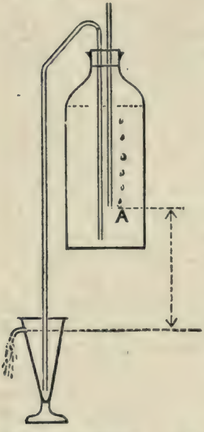


Fig. 20.—China Clay Analysis.

Analysis.—The complete analysis of clay is not required.

The total moisture is determined by igniting a sample in a platinum crucible and calculating the loss of weight in the usual manner. The moisture normally present does not usually exceed 15 per cent.

Iron.—The clay may be extracted with a little hydrochloric acid, and the solution tested colorimetrically for iron. It is present in all clays, but often in traces only. Any iron which cannot be extracted with hydrochloric acid need not be taken into consideration, as it can hardly get into a soluble state in the beater.

Ultramarine added, to blue the clay, may be detected under the microscope, but care must be taken to distinguish it from bluish particles arising from natural

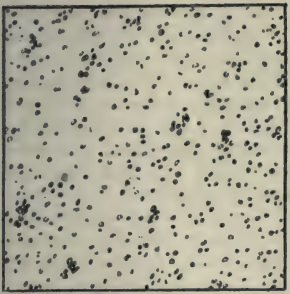


FIG. 21.—China Clay. Particles very uniform in size (under low power).

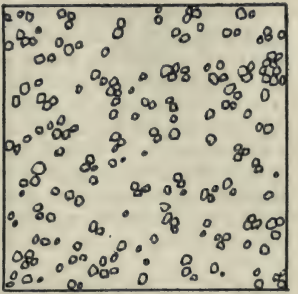


FIG. 22.—China Clay. Same sample as shown in fig. 21 (under high power).

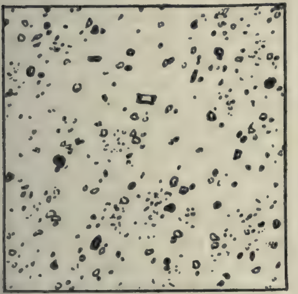


FIG. 23.—China Clay. Described as "Natural."

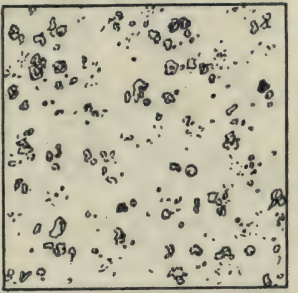


FIG. 24. — Micaceous Particles from China Clay.

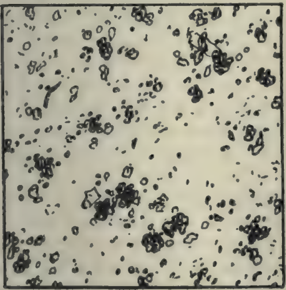


FIG. 25.—China Clay with Micaceous Particles.

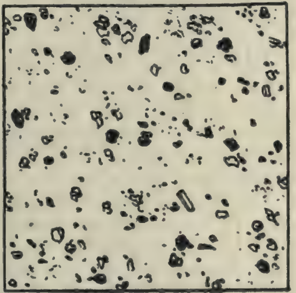


FIG. 26.—China Clay. Inferior Quality.

coloured veins, sometimes found in china clay deposits. Any quantity of ultramarine is detected by moistening the clay with acid, when sulphuretted hydrogen is given off. The odour of the gas, which resembles rotten eggs, is very characteristic. It also produces a metallic stain on filter paper dipped in a solution of silver nitrate.

Coal-tar dyes, added for the same purpose, are not so easily detected; it is best to shake out the clay with alcohol, in which dyes are usually soluble.

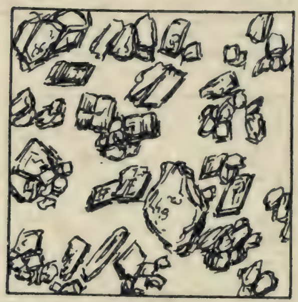


FIG. 27.—Ground Barytes (under high power).

BARYTES AND BLANC FIXE.—These substances are forms of barium sulphate; the barytes being merely a mineral substance ground up and purified by levigation (fig. 27), while blanc fixe is artificially prepared by treating a solution of barium salt, generally the chloride, with sulphuric acid or aluminium sulphate. Owing to its high specific gravity (4·6) it is not satisfactorily retained by pulp in the beater, but it is well adapted for use as a mineral coating for art papers. It is usually sold as a paste. It should be examined for moisture, soluble matter and mineral adulterants. The aqueous extract should also be tested for residues of mineral acid left in the "blanc fixe" in cases where the precipitate has not been thoroughly washed. If acid be found its amount may be determined by titration with $\frac{N}{10}$ alkali in the usual manner. Excess of acid has a deleterious effect on the adhesive used in making mixtures for coating papers, as, for instance, it precipitates solutions of casein by neutralising the alkali used to dissolve the latter and causing the whole mass to thicken and clot.

Mineral adulterants, such as chalk and other lime salts, are detected by digesting 5 grams of the substance with diluted hydrochloric acid. The residue left over from the determination of soluble matter may be used for this purpose. The hydrochloric acid extract is tested for lime by adding a slight excess of ammonia, filtering if necessary, and adding ammonium oxalate solution to the filtrate when any calcium present will be precipitated as oxalate. If any quantity of lime is detected it may be estimated by exhausting 5 grams several times with hydrochloric acid, uniting the filtrates and neutralising with ammonia as before. The clear alkaline solution filtered from any insoluble matter is precipitated with an excess of ammonium oxalate, the liquid heated to boiling and filtered off, collecting the precipitate on a filter paper and washing with hot water until free from ammonium oxalate. This may be ascertained by testing a little of the filtrate with a drop of calcium chloride solution, which gives a precipitate as long as any oxalate is present. The precipitate of ammonium oxalate may be strongly ignited in a platinum crucible and weighed as calcium oxide (CaO), or it may be dissolved in warm dilute sulphuric acid and titrated with $\frac{N}{10}$ permanganate. In the latter case the precipitate may be washed off the filter paper into a beaker by a jet of hot water, sulphuric acid added, the contents of the beaker heated to about 60° C., and permanganate run in from a burette. Permanganate is added slowly at first, and then more rapidly as fast as it is decolorised. The addition is continued until a faint permanent pink colour is obtained. When the end point is reached the filter paper on which the calcium oxalate was filtered and washed, and which still contains traces of calcium oxalate adhering to it, should be put into the beaker, when it will be generally found that a few more drops of permanganate are necessary to obtain the permanent pink tinge. Each c.c. permanganate = ·0028 gram of calcium oxide (CaO), or ·005 gram of calcium carbonate ($CaCO_3$).

Gypsum, Terra Alba, Annaline, Pearl Hardening or Crown Filler.—These are all forms of calcium sulphate in combination with 2 molecules of water, thus $CaSO_4 2H_2O$, sp. gr. 2·2 to 2·4. As calcium sulphate is appreciably soluble in water, that is to the extent of about ·2 to ·3 per cent., there is always a considerable loss if it be used for loading in the beater.

Gypsum and "terra alba" (fig. 28) consist of the ordinary mineral ground. Annaline is a natural fibrous form of gypsum ground and powdered. Under the microscope it is seen to consist partly of minute needles or rods.

"Pearl hardening" (fig. 29) or "crown filler" consists of calcium sulphate artificially prepared by precipitation in a similar manner to blanc fixe.

SATIN WHITE.—This is an artificially prepared mineral for coating, consisting of precipitated calcium sulphate and alumina, prepared by grinding together the necessary proportions of alum and slaked lime, with sufficient water. It is usually sold as a paste, the quality depending upon the evenness and fineness of the particles. The moisture in the paste may be determined in the usual manner. An aqueous extract should also be prepared and tested for reaction to litmus. Samples should not react strongly alkaline, as this points to faulty manufacture, either through the use of too large a proportion of lime or through inefficient grinding and interaction between the lime and alum. It is largely used for coating papers.

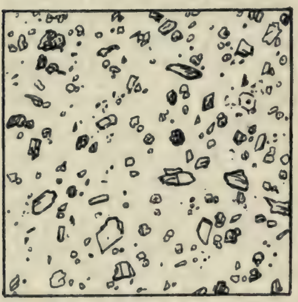


FIG. 28.—Terra Alba.

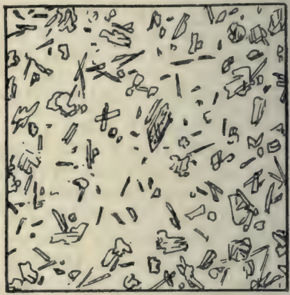


FIG. 29.—Pearl Hardening.

ASBESTINE, AGALITE AND POWDERED TALC.—These substances consist chiefly of magnesium silicate, and are insoluble in water. Sp. gr. 2·2 to 2·5. Asbestine is a finely divided form of asbestos, the particles are needle-shaped and retained to a large extent by the pulp when added direct to the beater. It forms one of the best materials for loading in the beater.

Agalite (fig. 30) resembles asbestine (figs. 31 and 32), although inferior qualities frequently contain irregular shaped particles as well as the before-mentioned needles. Samples of these minerals should be microscopically examined, and the proportion of needle-shaped particles noted. Inferior qualities will contain a large proportion of irregular shaped lumps resembling kaoline. Agalite contains at least 90 per cent. of magnesium silicate, asbestine 95 to 97 per cent.

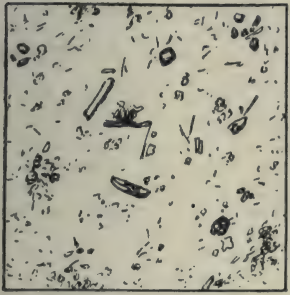


FIG. 30.—Agalite.

FIG. 31.—Asbestine (under low power).

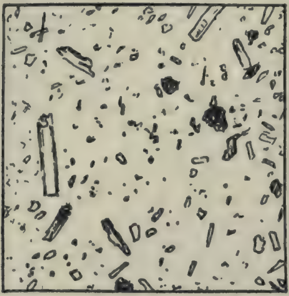


FIG. 32.—Asbestine (under high power).

DIATOMITE OR TALITE, an infusorial earth, is also sometimes used as a filler. There are considerable deposits in Ireland and on the Continent. It is of a dull white shade and very bulky owing to the irregular shape of the particles.

Further details *re* analysis and identification of mineral loadings will be given in Chapter VII.

MINERAL COLOURING MATTERS.

Some of the most important mineral colours are :—

Blues.—Smalts, ultramarine, Prussian blue.

Yellows.—Ochres, chromates of lead.

Reds.—Various oxide of iron reds, such as Indian red, Venetian red.

Greens.—Green ultramarine. Mixtures of the above blues and yellows, except ultramarine and lead chromate.

Browns.—Manganese brown. Umber.

Many of these colours are advantageously produced *in situ*, that is, precipitated in the pulp by adding the necessary chemicals—see next chapter on manufacturing operations. Colours like minerals are sold either in the dry state or in paste form ; in the latter condition they must be kept in well-closed vessels, or they may cake and are then difficult to dissolve. Moisture may be estimated both in the dry and paste colours as already described for china clay. Colours may be adulterated with numerous mineral and organic substances. This particularly applies to the more expensive colours, especially when in paste form. The addition of white minerals, such as ground barytes, clay, gypsum, etc., lowers the intensity of the colour, and may be best detected by comparative tests of colouring power. The presence of soluble organic substances such as glycerine and syrup may be detected by extracting the colour with successive quantities of hot water. The aqueous extracts are concentrated and tested.

Syrup is usually detected by Fehling test. The reagent consists of two solutions which are mixed in equal quantities before adding the substance to be tested. The solutions should be preserved in separate bottles. Solution A is prepared by dissolving 69·3 grams of pure recrystallised copper sulphate in 500 c.c. of water. A drop or two of dilute sulphuric acid may be added to the solution if it is not quite clear. Solution B is prepared by dissolving 350 grams of Rochelle salt and 100 of caustic soda in separate portions of water, mixing and making up to 500 c.c. A drop of the liquid suspected to contain syrup is added to a test tube containing half a c.c. each of the solutions A and B. The mixture is gently warmed, and if syrup be present the sugar it contains brings about a reduction of the copper sulphate, forming a yellowish-red precipitate of cuprous oxide.

Glycerine cannot be identified by simple tests, but its presence may often be detected by the peculiar smell produced when it is strongly heated.

Determination of Colouring Power.—This is best done by mixing the colours in various proportions with a quantity of fine white mineral such as china clay. In all cases a sample of good genuine colour must be taken as a standard for purposes of comparison. One part of the colour may be intimately mixed with five or ten parts of china clay, and the intensity of the colouring compared with a similar mixture using the standard colour. The best proportion of china clay to take for the test will depend upon the colouring power of the material under examination. The test may be made quantitatively by first mixing one part of a standard colour with, say, ten parts of china clay, then taking one part of the colour under examination and mixing with china clay, increasing the quantity of the latter until the intensity of the colour of the two mixtures is equal. The colouring power of the sample under examination may be expressed in terms of the relative amount of china clay required as compared with that taken for mixing the standard colour. The value of a mineral colour depends very largely on the state of division. The more finely divided the colour the more deeply it will colour the china clay in the above tests and the pulp in the beater. It should be borne in mind that all the mineral colours now under consideration, act not only as colouring matters but also as loading, and therefore the considerations which apply to china clay and loading materials also apply to mineral colours.

The more plastic the material the better the result obtained, and all colours should be free from grit and sandy particles. These may be tested for by spreading a little of the colour on a sheet of paper and pressing with the blade of a knife, or by rubbing up a little of the colour moistened with water with the finger on a sheet of glass or other smooth surface.

Ultramarine.—This is perhaps one of the most useful blues known to the papermaker, as there is no better colour for counteracting the natural yellowish shade of bleached fibre. It owes its superiority largely to the fact that it is the purest permanent blue pigment known. It varies, however, considerably in shade and also in intensity of colour, and its colouring power should be tested as already described. Erfurt directs that one part each of the sample under examination and the standard colour should be mixed separately with five parts of china clay and made into a paste with equal parts of water. The sample which shows the deepest shade contains the strongest ultramarine.

Ultramarine is more or less sensitive to the action of acids according to the method of manufacture and composition. The colour of some samples, especially those of a violet hue, is rapidly discharged by alum. Such varieties are unsuitable for papermakers' use. To test the power to resist the action of alum, a portion of the sample is agitated in a clear glass vessel with a 5 per cent. solution of aluminium sulphate, and its behaviour compared with that of a sample of standard ultramarine under exactly the same conditions. Some samples are rapidly decolorised in this manner. Erfurt considers that no appreciable alteration of shade should be apparent after the ultramarine has stood half an hour in contact with the alum solution.

Ultramarine, although sensitive to acids, is very little affected by alkalies. On the other hand, Prussian blue is unaffected by strong acids but rapidly decolorised by alkalies. Unfortunately Prussian blue is of too greenish a hue to allow of its replacing ultramarine in counteracting the natural yellowish colour of bleached pulp. Coal-tar dye substitutes for ultramarine are the various indanthrene and duranthrene blues mentioned later.

Smalts consist of a cobalt glass ground and finely powdered. It is a permanent blue colour unaffected either by acids or alkalies; unfortunately its colouring power is weak, and it is as a rule far too expensive for the papermaker. On account of the colour being unaffected on exposure to light, it is occasionally used in high class hand-made ledger and such like papers.

Prussian Blue. This colour is produced by the interaction of solutions of yellow prussiate of potash (potassium ferrocyanide) and copperas under the oxidising influence of the air with or without the addition of alum and sulphuric acid, the shade of colour depending on the proportions and methods of preparation. The papermaker will probably buy his blue ready made in paste form, or if he prefers to make it himself it is in most cases better to precipitate the colour in the pulp rather than produce the blue separately, then adding it to the beater. It is not only less trouble to produce it in the pulp, but the colour is retained to a larger extent, and is found to be more permanent to light.

Although Prussian blue is not affected by the generality of acids, it is noteworthy that it dissolves in oxalic acid and its salts. Alkalies immediately discharge the colour precipitating the iron as ferric oxide and reforming prussiate of potash. When the reaction is carried out in a test tube and acid added in sufficient quantity to neutralise the alkali the blue is completely reformed, and this will hold good in the beater, provided that the prussiate of potash liberated by an alkali is not washed away before acidifying.

RED AND YELLOW IRON PIGMENTS.—There are a number of permanent mineral colours both of natural and artificial origin and of various shades, from golden yellow to red and brown, of which iron in the form of oxide or hydroxide is the basis. The natural earth colours of this class include the ochres, such as golden ochre, Roman ochre, brown ochre, etc., and consist essentially of hydrated oxide of iron generally accompanied with alumina. The amount of oxide of iron averages about 12 per cent. Closely allied and of similar composition to the ochres are the sienna earths; the unburnt earths are yellow, the burnt earths red. Red mineral colours such as Indian red, Venetian red, and other oxide reds, differ from the ochres in that the colouring principle consists of ferric oxide in the anhydrous condition, while that in the ochres is hydrated. Many are of natural origin, principally the ground product from red hæmatite ores. Others are obtained by calcining ochres and other clays containing a considerable amount of iron, the colour of the product depending upon the percentage of the latter. I may remark in passing that the red or yellow colour of ordinary bricks is due to the iron originally contained in the clay. The red mineral colour, known as "caput mortuum," is obtained as a by-product in heating copperas. The more modern oxide colours are produced from the waste iron liquors, such as the acid liquors obtained in the process of pickling sheet iron previous to the operation of tinning or galvanising. The acid liquors are precipitated with the cheapest alkaline substances to hand ; with due care even lime may be used. The precipitate of oxide of iron is collected on filters and calcined. In this manner pigments with a wide range of colour can be produced, and they are preferred to the natural ground mineral earths, as they are mostly brighter in colour and freer from coarse particles and grit. Brown pigments of this class consist largely of hydrated oxide of iron ; the natural colours known as umbers are obtained by calcining the natural earths which are known as raw umbers and are of a greenish shade. They differ in a chemical sense from the colours already discussed, as they contain on an average 10 to 12 per cent. of manganese oxide in addition to about 30 per cent. of oxide of iron. Artificial umbers or manganese browns are prepared from waste liquors, the so-called still liquors obtained in the production of chlorine for the manufacture of bleach.

YELLOW AND ORANGE CHROMES.—The chrome yellows and chrome orange form an important group of yellow mineral pigments of artificial origin. They are bright yellow to orange in colour, and although somewhat less permanent than the ochre and iron oxide pigments, they are yet found in practice to be permanent, in contrast with the coal tar dye colours now so much used. The instability of the chromes is due to chemical reduction in the presence of organic matter. They are also very susceptible to the action of sulphur compounds and may consequently blacken when exposed in a situation where much coal gas is burned and should not be used in conjunction with sulphur containing substances such as ultramarine. Chemically they consist of a mixture of normal and basic lead chromates. One of the disadvantages attending their use is their poisonous nature. They are prepared by wet methods—a solution of sugar of lead (lead acetate) or nitrate is mixed with sodium or potassium bichromate. The colour obtained depends on the proportion in which the solutions are mixed and may also be modified by the addition of Glauber's salts (sodium sulphate). As in the case of Prussian blue, the papermaker will probably prefer to produce the colour in the pulp if he decides to make his own colour, especially as the specific gravity of lead chromate is high (5·6), and a large proportion of the mineral will be lost if added directly to the pulp. The colour as bought is very liable to adulteration with china clay, barytes, gypsum, chalk and similar substances. Samples should be examined for fineness of particles, as described under china clay. Most of the above minerals will contain traces of larger particles and grit. The samples should also be tested for colouring power, as described under ultramarine. Lead chromates are completely decomposed by heating with strong hydrochloric acid, and any undissolved mineral residue points to the addition of an adulterant, probably barytes or china clay. The solution should be filtered while hot and the residue washed with hot dilute hydrochloric acid and then with boiling water to free it from lead salts. The residue dried and weighed will give the percentage of barytes and china clay. To detect and estimate gypsum, dissolve 2 grams in hydrochloric acid, add dilute sulphuric acid and allow to cool. The solid residue will consist of lead, as sulphate or chloride, and barytes and china clay, while the gypsum will be contained in solution. The precipitate is filtered off and ammonia added in slight excess; any further precipitate is again removed by filtration and the clear liquid treated with a solution of ammonium oxalate. If any calcium derived either from gypsum or chalk be present, a precipitate of calcium oxalate will be formed. This precipitate can be filtered off, washed and the calcium estimated as described on page **117**. If the original colour effervesces when treated with acid it probably contains chalk added in some form or another.

Black Colours.—The commoner black colours such as lamp-black are not very suitable for colouring pulp, on account of their mode of production. They are produced by burning oily or resinous refuse and allowing the black soot to deposit; such soot always contains oily or greasy matter. On the other hand, certain forms of carbon black obtained by charring twigs or similar matter, such as Frankfort or drop black, may be used. I may also mention the so-called Prussian black obtained by calcining Prussian blue. In cases, however, where it is desired to produce the black colour in the pulp, it is generally preferable to treat the pulp direct with a ferric salt, such as nitrate of iron and tannin, as described in the next chapter.

Ammonia Solution.—A strong solution of ammonia gas (NH_3) in water is occasionally required, as, for example, dissolving casein in the manufacture of coated papers. In most respects a solution of ammonia behaves like one of caustic soda, but is milder in its action, and being volatile there is less danger of using too much of it—the excess that has been added gradually evaporating and disappearing from the paper. The concentrated liquor, as usually sold, has a sp. gr. of ·880 and contains 35 per cent. of ammonia gas. Great care must be exercised in handling the strong ammonia liquor, especially in hot weather. When removing the stopper, especially when opening a fresh bottle, stand it firmly on a low table and keep the face averted in case of any of the liquor spirting out. Needless to say it should be stored in a cool place.

It is not usually necessary to determine its strength, but this may be done by titrating the strong liquor diluted to a convenient strength with standard acid, using methyl orange as an indicator.

Copper Sulphate or Blue Stone.—This substance consists of well-formed crystals of fine blue colour, consisting of the hydrated salt ($CuSO_45H_2O$). It is used in small quantity for fixing some of the coal-tar dyes on paper pulp.

Borax or Sodium Biborate.—This is the sodium salt of boracic acid ($Na_4B_2O_7$), and forms large colourless crystals. It is readily soluble in water, the liquid having a mild alkaline reaction. Like sodium carbonate and ammonia it is an excellent solvent for casein.

Sodium Chloride or Common Salt.—This substance (NaCl) may be obtained in crystals or blocks containing only traces of impurities, mostly magnesium salts, owing to which it is slightly hygroscopic. It is used in conjunction with some of the coal-tar dyes for colouring paper pulp.

Zinc Sulphate.—This substance is sold in the form of small white crystals strongly resembling Epsom salts. It is used in sizing with viscose, to precipitate the latter in the engine in the place of alum in ordinary rosin sizing.

Mordants or Fixing Agents for Colouring Pulp.—Many coal-tar dyes and dyes of vegetable origin require the use of a mordant to fix the colouring matter to the fibres. They consist usually of well-defined chemical substances, of which alum is the most important. A short description of the others may now be given. Some of them also serve for colouring pulp directly by precipitating the mineral matter in the fibre.

ALUMINIUM ACETATE LIQUOR.—The solution required may be prepared by mixing three parts by weight of aluminium sulphate (15 to 16 per cent. aluminium) with two parts of lead acetate (sugar of lead). This results in a precipitate of lead sulphate, which is allowed to settle, the clear liquid being poured off for use. A further addition of 5 or 6 per cent. of soda crystals on the weight of aluminium sulphate used is recommended in order to neutralise any free acid.

POTASSIUM AND SODIUM BICHROMATES occur in bright orange crystals readily soluble in water, the sodium salt being cheaper and more soluble than the potassium salt. Insoluble brown colours are produced with the aid of catechu and the subsequent addition of bichromate. Bichromate, when mixed in certain proportions with sugar of lead and sodium sulphate, yields various shades of yellow and orange chromes already mentioned.

COPPERAS OR FERROUS SULPHATE.—This substance is used for producing buff-coloured iron compounds in pulp. It precipitates substances such as logwood and catechu, and dulls the tone of (saddens) the brighter basic coal-tar colours. It is prepared by heating scrap-iron or pyrites with sulphuric acid, the green crystals of copperas separating out from the liquor.

"NITRATE OF IRON" OR FERRIC SULPHATE.—The liquor is obtained by oxidising ferrous sulphate or copperas with nitric acid; in the course of the chemical reaction which ensues the nitric acid is mostly decomposed, so that chemically the liquor consists of ferric sulphate. It may be prepared (Erfurt) by gradually adding 15 parts of copperas to a mixture of 2 parts sulphuric acid (168 Tw.) and 3 parts nitric acid (64 Tw.) diluted with 6 parts of water in a large glazed earthenware vessel. The copperas must be added gradually, or the reaction may become too violent, causing the liquor to froth over; the liquid should be stirred from time to time, and the operation should be conducted in the open, as the red fumes produced are poisonous. After all the copperas has been added and the evolution of gas has slackened, the liquor should be heated to boiling for a few hours with live steam with the addition of some clean iron borings.

A large excess of acid must be avoided, as it would tend to rot the fibre, although of course the liquor will always react acid to test papers. Any large excess of acid may be neutralised by the addition of a little soda after mordanting the pulp.

ACETATE OF IRON OR BLACK IRON LIQUOR.—This serves a similar purpose to the "nitrate of iron," and is obtained by dissolving clean scrap iron in crude acetic acid (pyroligneous acid). The acid should be completely saturated, for which purpose an excess of iron should be used. It is more expensive than nitrate of iron.

TANNIC ACID OR TANNIN, a mixture of gallotannic acid and similar substances, which occur naturally in numerous plants, such as oak galls, sumach, myrobalans, gambier, cutch, etc., from which an extract is obtained.

This substance is of considerable value in dyeing and mordanting paper pulp, in virtue of the dark-coloured compounds it forms with iron salts. It is, further, an excellent mordant on account of its affinity for the vegetable fibre.

The percentage of tannin contained in the different raw materials differs considerably.

COAL-TAR DYES.--Even a brief description of the chemistry of these substances would occupy much space and would not be intelligible to any but those having a considerable knowledge of organic chemistry. The use of coal-tar colours, however, is so general that I shall attempt a short description of their nature and behaviour, but only so far as is necessary to enable the mill chemist to detect commoner adulterants, and to make comparative tests of solubility, colouring power, etc.

Coal-tar colours are substances of complex composition and belong to one or other of a limited number of types, many dyes of the same type being closely related to one another and having the same general properties. The differences between dyes lie, therefore, not only in a difference of colour and solubility, but frequently in a difference of chemical nature, which is apparent in the relative ease with which they are retained by the pulp. Vegetable fibres as used in papermaking do not as a rule take dye so well as animal fibres, such as wool and silk, so that many dyes that can be used for the latter substances are quite useless to the papermaker. I shall for the present confine myself to the chemical properties and adulteration of dyes. The best dyes to use for different purposes are given in Chapter VI.

Like other chemical substances coal-tar dyes may be of acid, basic or neutral character, and consequently they may form salts with inorganic acids or bases. These salts may also combine with other inorganic salts to form double salts similar to such inorganic counterparts as yellow prussiate of potash or ammonia alum. Many of the dyes as sold and used consist of salts or double salts of this nature. From the chemical point of view the following rough classification is useful :—

1. *Basic Colouring Matters.*—These dyes consist not of the dye base which is frequently colourless but of the salts of the base. By the term dye base is understood the organic compound which may be regarded as a complicated derivative of ammonia, and, like ammonia, having alkaline or basic properties and combining with acids to form salts. In these cases the colouring matter consists of the salts which are frequently the hydrochlorides, but may also be nitrates, acetates, etc. Such salts are simply produced by bringing together the dye base with the corresponding acid. As an illustration of the differences between the different salts of the same dye base, I may mention fuchsine acetate which is more easily dissolved than an ordinary diamond fuchsine, and therefore better adapted for some purposes, although the higher price of the acetate somewhat counterbalances this advantage.

2. *Acid Colouring Matters.*—It is necessary to divide acid colouring matters into two classes; the first class consisting of ordinary organic dye compounds which are of an acid nature; secondly, those which owe their acid nature to the sulphonic acid group (SO_3H).

Taking first the ordinary acid colouring matters, these are organic acids which, however, are too insoluble in water for ordinary use. On the other hand, the salts produced by combining them with alkalies are readily soluble, and therefore suitable for use. These acid colouring matters often contain the elements chlorine, bromine and iodine, or else the so-called "nitro" group

(NO_2) usually produced by treating with nitric acid. Many of these acid colouring matters unite with the hydroxides of aluminium, tin, iron, chromium, etc., to form the lake colours. This action is also brought into play when aluminium hydroxide is precipitated on the fibre by reaction between the alum and the size in the beater. The second group of acid colouring matters, the sulphonic acids, differ from the others in that the acids themselves are soluble in water and can be used direct. They are prepared from the foregoing basic or acid colouring matters by sulphonating (treating with strong sulphuric acid). The process of sulphonation has but little influence on the colour of the dye, but it is a means frequently employed by the colourmaker in order to obtain dyes easily soluble in water.

3. *Neutral Colouring Matters.*—To this class belong colouring matters having neither basic nor acid properties. This is a comparatively small class, of which indigo is the most important member.

Analysis.—Coal-tar dyes are very generally adulterated; how general this adulteration is may be gathered from the following extract from the journal of the Society of Dyers: "Adulteration is so generally practised that the pure colouring matters are almost unknown commercially." The adulteration consists in the addition of inert matter to the dye with which it is thoroughly incorporated. The proportion of dye to adulterant, what is termed the standard of strength, may in some cases be as low as 2½ per cent.; that is to say, the dye as sold only contains 2½ per cent. of actual dye substance. The adulterants consist of a number of both organic and inorganic substances, the commonest of which are common salt, Glauber's salt (sodium sulphate) and dextrine, a substance produced from starch; in addition the following are frequently used: Epsom salts (magnesium sulphate), oxalic acid and some of its salts, starch, sugar and glucose. The sample of dye for examination, especially if a paste dye, should first be tested for excess of moisture. Two grams are carefully weighed out and dried at 100° to 110° Centigrade until no further loss of weight takes place. The sample may be further tested for adulterants by grinding up and adding small portions of warm water to the powder in the mortar, pouring off each time through a filter paper, till all soluble matter is washed out, the residue of insoluble matter being finally transferred to the filter paper, which is dried and weighed, the weight giving the amount of insoluble adulterants. Instead of weighing the mineral residue, an aliquot part of the filtrate may be evaporated to dryness in a tared dish. From this the total weight of soluble matter is calculated. By deducting the soluble matter from the total amount of dye originally taken the amount of insoluble matter is determined. This latter method has the advantage that it obviates any inaccuracy about weighing the filter paper which holds the solid residue. Of course, the soluble portion will contain any adulterants soluble in water, such as salts, sugar, etc.

Dye stuffs are very frequently soluble in strong alcohol, whereas mineral salts, sugar, starch, etc., are insoluble. This fact may be made use of to separate dye from adulterants. It is only necessary to digest the sample with repeated quantities of alcohol, pouring off each time until the colour is removed, leaving the adulterants behind, which are then dried and weighed. Some idea of the mineral adulterants can be got by burning a sample of the dye and determining the percentage of ash. This method would be quite reliable were it not that many dyes, as already explained, consist of metallic salts or double zinc salts of the actual organic dye compound.

A part of the ash should be dissolved in water and tested for chlorides. A large quantity of chloride will probably point to adulteration with common salt. On the other hand, a trace of chloride may be due to the common salt used in the process known as salting out. Further, eosine and similar dyes contain halogens (chlorine, bromine and iodine), which find their way into the ash, yielding a soluble chloride, bromide or iodide and a precipitate with silver nitrate. In case of doubt the eosine dye is first extracted from an acid solution by means of ether, and the aqueous solution concentrated and burned to ash.

A solution of the ash may also be tested for sulphates with barium chloride solution. Here again the presence of sulphates must not be taken as proof of adulteration with Glauber's or Epsom salts without further investigation, as a sulphuric acid may have its origin in the sulphonic acid group present in the dye. The following method may be adopted. The solution of the dye is precipitated direct with barium chloride, the precipitate filtered off, washed and digested with a solution of ammonium carbonate, by which the barium sulphate is unaffected, whereas the barium sulphonate will be converted into barium carbonate. After pouring off the ammonium carbonate and washing with a little water, the precipitate is treated with dilute acid, which dissolves the barium carbonate, leaving any barium sulphate unacted upon.

If a considerable quantity of magnesium be detected in the ash, the presence of Epsom salts in the original dye may be regarded as certain. To test the ash for magnesium dissolve in a small quantity of hydrochloric acid, subsequently adding ammonia and ammonium chloride and ammonium oxalate ; the solution is filtered and the filtrate tested with sodium phosphate, which gives a precipitate in the presence of magnesium salts. To determine dextrine, dissolve out the dye with strong alcohol and take up the residue with a very small quantity of water in a tared beaker with a glass rod. Add alcohol in small quantities at a time until no further precipitate is formed. The dextrine on separating adheres to the side of the vessel, so that clear liquid may be poured off. The beaker is rinsed out with a little spirit, dried at 100° C. and weighed ; the difference between this and the original weight of the beaker gives the additional weight of the dextrine.

Sugar is left after exhausting the dye with strong alcohol ; the residue is taken up with water and filtered. Sugar may be detected in the filtrate by means of Fehling solution (see p. 120).

Starch is left in the residue after extraction with alcohol and cold water. It may be dissolved in warm water and tested with iodine solution, when the well-known blue colour is produced.

We have hitherto spoken of various substances contained in the original dye as adulterants, but as already pointed out this form of adulteration is exceedingly common, and has become so general in the trade that objection cannot be taken to samples on such grounds. It is, however, of extreme importance for the papermaker to form some opinion of the standard of strength of the material he uses. This may be done to a certain extent by testing for adulterants as just described. In many cases, however, it is much quicker and more satisfactory to determine the colouring power of the sample, provided that a genuine sample of known qualities can be procured as a standard. The simplest method of doing this consists in dissolving equal quantities of the standard and of the sample to be tested in water, and comparing the intensity of the coloured liquids so obtained. It is usually sufficient to take 1 gram of the dye making the solution up to 1 liter, but great care must be exercised to see that every particle of dye is dissolved. It is better to put the dye into a beaker, dissolving it in successive small quantities of water, pouring off each time into the liter flask, finally making up to the mark and mixing well, just as described in preparing the standard solution of iodine solution. The solutions so prepared are poured into separate Nessler glasses, and the depth of colour compared. It may be better in the case of some of the purer samples to dilute the solution still further before comparing colours, as the relative intensity of the colours is not easily seen unless the solutions be very dilute. If the colour in one tube is found to be stronger than in the other the relative intensity may be judged by pouring away small quantities out of the tube containing the stronger colour, until the intensity of both are the same when looked through from above. Further tests may be made by digesting equal quantities of unstoved white woollen yarn in a liter of each solution, the liquids in both cases being gradually heated to 80° C. and then to 100° C. for half an hour. After this treatment the samples of wool are removed from their respective solutions and the tints compared.

When a colour is ordered to any special shade it is often impossible to know whether it is homogeneous or consists of a mixture of two or more colours. Mechanical mixtures of this sort may be detected by sprinkling a very small quantity of the powder on a piece of filter paper and floating it on water or alcohol. The liquid immediately penetrates the paper and each spot of dye produces a stain, so that in the case of a mixture of dyes, different coloured stains appear on different parts of the paper. With care and experience it is possible to estimate roughly the relative proportions. If, however, the dyes resemble one another closely in shade this test will fail, but the difficulty may be got over by sprinkling a little on the surface of strong sulphuric acid in an open dish ; in all probability the dyes of similar shades will be of a different nature and will therefore produce different colours in the strong acid. Actual mixtures are thus distinguished from dyes ordered to shade. A method of capillary analysis may also be used. The dye under examination is dissolved in water and placed in the dish of the "bibliometer," and the rate at which the dye mounts in a strip of blotting paper is determined. This will be found to vary with different dyes and is useful for purposes of identification. Further, if the sample under examination is a mixture of two dyes they will probably rise in the strip of paper at different rates with the result that one will overlap the other on the lower part of the strip only, while at the upper end the colour with the greatest capillarity will appear alone. Actually it is a question of the retention of the dye by the fibre (adsorption). The dye which is most readily retained is first removed as the solution rises in the strip of paper, the colour appearing at the upper end being that of the dye which is least readily fixed by the fibre.

I have made no attempt to explain how different dyes can be identified chemically ; the subject is a complicated one and can only be tackled by a chemist of considerable experience. The difficulties are increased by the fact that the chemical differences between dyes of the same class are very small, and, further, that most dyes go under several names not only chemically but also in the trade. In the next chapter will be found a list of the best dyes adapted for colouring pulp with directions for applying them.

CHAPTER VI.

FIBROUS RAW MATERIALS—HALF-STUFFS AND THEIR TREATMENT.

ISOLATION OF PAPER-MAKING FIBRES.

Character of Cellulose.—Cellulose is a general term applied to the chemical substances forming the basis of paper-making fibres. There are numerous types of cellulose having different compositions and properties according to the raw materials from which they are isolated; thus, the more resistant forms of cellulose forming the fibres used in paper-making are not identical but only related to one another.

From a chemical aspect the prepared fibres or half-stuff may be grouped into three classes:—

1. The "normal" celluloses, *i.e.* cotton, linen, hemp and ramie. These resemble one another closely and give the same chemical reactions. Whether they are actually identical or not cannot be stated with certainty. This form of cellulose may be termed the normal cellulose, or cellulose par excellence; it is the most resistant to the action of the air and chemical reagents, and consequently forms the most permanent basis for the manufacture of paper.

2. The cellulose of straw, esparto, bamboo, etc. These celluloses differ from the foregoing in containing a larger proportion of oxygen; they are therefore termed oxycelluloses. In their chemical reactions they differ markedly from the normal cellulose. The oxycelluloses are widely diffused in nature and form the basis of most of the fibrous tissues of plants.[1]

---

[1] For a full account of the chemistry of cellulose, see *Cellulose* and *Researches on Cellulose*, by Cross and Bevan.

3. The celluloses derived from lignocellulose : This type of cellulose is an oxycellulose and occurs in raw jute and wood fibres in combination with bodies belonging to the aromatic series in the form of lignocellulose. In addition to the oxycellulose, termed α-cellulose, lignocellulose contains a second cellulose or β-cellulose, characterised chemically by the presence of methoxyl groups. β-cellulose is less resistant to the action of hydrolytic agents than α-cellulose and is mostly broken down in the manufacture of chemical pulp from wood.

The less stable nature of the oxycellulose as compared with the normal cellulose is evidenced by the fact that when heated it is gradually oxidised, absorbing oxygen from the air. Thus, in an air bath at 100° C. chemical pulp undergoes gradual oxidation, as will have been noted by anyone who has observed the increase in weight of wood pulp if left in the oven after all the moisture has been driven off. For this reason the varieties of oxycellulose when converted into paper, that is to say, such fibres as are isolated from wood, straw, esparto, etc., may not be found so lasting or permanent, even when carefully prepared, as the fibres contained in cotton and linen papers that have stood for centuries.

Isolation of Fibres.—Raw fibrous material is examined to determine the percentage of "cellulose" it contains, that is to say, the percentage of resistant fibres suitable for paper-making which would be obtained in manufacturing processes for the production of paper pulp. From what has already been said, it will be realised that the yield of cellulose will differ according to the process employed, whether on a large scale or in the laboratory. In the process of removing what are often termed "encrusting matters" the chemical reagents attack the more resistant cellulose to a certain extent, thus reducing the yield of "cellulose." In cases where drastic treatment is necessary to remove the encrusting materials there will be a greater loss of paper-making fibre.

Before applying the necessary reagents the raw material is examined to see if the crude fibres are lignified or not. There are numerous methods by which lignocellulose may be identified. Some of the colour reactions are given later. I may here mention the action of aniline salts, producing a yellow colour and ferric-ferricyanide reagent (Cross and Bevan), depositing Prussian blue in the fibre. This latter reagent is made by bringing together solutions of ferric chloride and potassium ferricyanide in equivalent proportions (1·62 to 3·3 by weight in 200 c.c. water). In addition there are a whole host of coal-tar dyes, especially basic dyes, which have a great affinity for lignocellulose, readily staining it. The most generally useful process for isolating cellulose is as follows :—

Yield of Cellulose or Paper-making Fibre.—The raw material is teased out or otherwise disintegrated without damaging the fibres, in order that the reagents to be employed may thoroughly permeate it. Three grams of fibre thus prepared are dried at 100° and weighed in a stoppered weighing bottle and then placed in a porcelain basin containing 1 per cent. solution of soda and heated for half an hour. The basin is covered with a large clock-glass to prevent undue evaporation and concentration of the solution or the loss made good from time to time by the addition of hot water. The fibre is then removed to a filter, either of calico or fine machine wire, and washed with water ; it is then squeezed to remove excess of the latter, and treated with chlorine gas. Small quantities of chlorine for this purpose are conveniently prepared by the action of strong hydrochloric acid on potassium permanganate. The latter is placed in a flask (fig. 33) provided with a cork with two holes ; into one hole is fitted a stoppered funnel containing the hydrochloric acid, which is allowed to drop on to the permanganate in the flask ; into the other hole is fitted a glass delivery tube leading into a wash bottle containing a little water, and from thence the gas is conveyed by another tube to the bottom of a beaker, or any other upright vessel, containing the fibre. The corks, after boring, are impregnated with molten paraffin wax to resist the action of chlorine or the whole

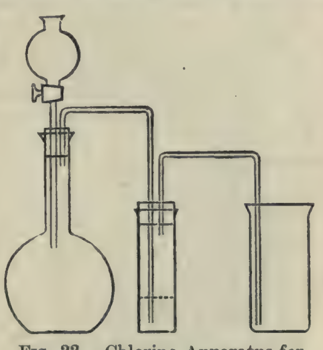


FIG. 33.—Chlorine Apparatus for Isolating Cellulose.

apparatus may preferably be made of glass with ground-in stoppers or joints in the place of corks.

Chlorine gas is of a yellow colour and heavier than air, and may therefore be seen gradually filling the beaker. The top of the beaker is covered as completely as possible with a clock-glass, and when full of chlorine the beaker is put aside to stand. After an hour or so, a little more chlorine may be introduced. Under this treatment the lignocelluloses turn a deep yellow colour owing to the combination of the chlorine with the aromatic constituent of the fibre with the production of a yellow chlorinated derivative. When the reaction is complete the chlorinated fibre is removed and placed in a basin with a 2 per cent. solution of sodium sulphite, and heated. The sulphite liquor and the chlorinated compound produce an intense purple colour which is destroyed on warming. After digesting for half an hour, the fibre is removed and washed with water. It should now present the appearance of well-bleached half-stuff. If it still contains yellowish or brownish specks it is a sign that the chlorine has not thoroughly done its work, and a second treatment is necessary. Repeated treatment should be avoided as far as possible, as the resistant cellulose is attacked and partially destroyed, giving a low yield. After washing, the isolated cellulose is dried at 100° C. and weighed in a stoppered weighing bottle ; this weight calculated on the original weight of the untreated fibres gives the percentage of cellulose. If lignocelluloses are absent, the treatment with chlorine may be replaced by treatment with sodium hypochlorite or ordinary bleach liquor.

Reference may be made to an ingenious method of estimating the amount of the lignine constituent in a sample of wood pulp or other lignified fibre based on the above reaction. Chlorine gas has also been used on a manufacturing scale for bleaching rag half-stuff, and the process is stated to be economical.[1]

There are several other methods of treating lignocellulose fibres in the laboratory for the isolation of cellulose, but they all yield a somewhat lower percentage, as the β-cellulose is attacked and rendered soluble. Chlorine may be replaced by treatment with bromine water (Müller), but several alternate treatments with boiling

---

[1] Beadle and Stevens, *Journ. Soc. Chem. Ind.*, 1914, 33, p. 729.

alkaline solution and bromine water in the cold are necessary. Another method (Schulze) is to digest the fibre for ten days or a fortnight with nitric acid, sp. gr. 1·1, containing ·5 per cent. to ·8 per cent. on the weight of the fibre of potassium chlorate. Nitric acid alone may also be used. The fibre is digested for two or three hours with three times its weight of 10 per cent. acid at 60° C. Red fumes are given off in quantity and the reaction should be carried out in the open air or in a fume cupboard.

Experimental Boiling.—The manufacturing operations may be still more closely followed in the laboratory with the aid of a digester (fig. 34). This consists of a strong metal vessel, to take a couple of quarts, provided with a cover which can be screwed down and fitted with a pressure gauge. There should also be a short tube closed at one end screwed into the cover to take the bulb and lower part of a thermometer. The tube should be partially filled with oil, so that the thermometer dips into it, forming an oil joint. In this way trial boils may be made on raw materials with soda. The volume and percentage strength of the liquor used is measured and a chart is made to register the temperature and pressure during the boil. These should be noted at least every half-hour to see that they remain constant when once the liquor is heated to the necessary temperature. At the completion of the boil the steam is blown off, the cover of the digester removed and the whole of the contents thrown on to a large sieve. The fibre when drained off is washed with further small quantities of water, the washings and residual liquor being mixed together and made up to a known volume; a portion of

FIG. 34.

the liquor is then analysed for total and free soda, as described under Rags.

The estimation of total soda, which should agree with the amount of soda originally taken, is a useful check on the washing process. The fibre, after thoroughly washing, is squeezed as dry as possible, weighed, and an aliquot portion dried at 100° C., and weighed in a stoppered weighing bottle. From this the total yield of bone-dry fibre may be calculated. The remainder may be bleached up, noting the proportion of chloride of lime required per 100 parts of fibre. The determination of the strength of the bleach liquor before use, and the residual chlorine in the liquor after use, is made with sodium arsenite solution, as already described.

Experimental boils may also be made with sulphite liquor; this should be of the strength and concentration described in the manufacture of wood pulp, where also will be found the method of analysing these liquors. The boil is carried out under the same conditions as when using soda liquors. When blowing off at the end of the boil a piece of rubber tubing may be connected to the blow-off cock and the gas led to the bottom of a Winchester quart bottle containing cold water, in order that the excess sulphurous acid may be absorbed and prevented from contaminating the air of the laboratory. As sulphurous acid attacks iron and even bronze to a certain extent, the interior of the digesters must be lead lined, as also the under surface of the cover. The gas also attacks the mechanism of the ordinary pressure gauge and a special valve is necessary. The boiled and bleached fibre may be made up into hand-sheets with a small hand-mould, but first requires to be disintegrated to separate the fibres and reduce it to the condition of pulp. For this purpose small experimental beating engines are built, and are very useful when it is required to get some idea as to the paper-making qualities of the fibre.

For rough purposes, where an experimental engine is not available, the boiled and washed material may be tied up in a stout rag and hammered. This usually succeeds in separating the fibres sufficiently to allow of the material being made up into rough hand-sheets.

If the quantity of pulp is not too large, it is placed in a strong glass bottle with glass or agate beads, and vigorously shaken in the same manner as when preparing a sample of paper for microscopic analysis. The sheets should be air-dried and may then be tested. The pulp may be previously rosin-sized or the sheets subsequently tub-sized and examined in a number of ways, as described in Chapter VII.

FIBROUS MATERIALS AND THEIR TREATMENT.

RAGS.—Rags are almost invariably bought by the papermaker in a roughly sorted condition, the type of rags depending upon his requirements.

The rags are then carefully sorted and cut either by hand or machinery. The sorting process is made according to fibre, that is to say, whether linen, cotton, hemp or woollen rags, and according to colour, namely, the various grades of white, grey, blue, red and, finally, all dark colours, including black.

For conversion to half-stuff, the rags undergo, in addition to sorting, the processes of cutting, dusting, boiling, breaking-in and bleaching. Tables have been compiled giving the loss of the different classes of rags in different processes, but as rags cannot be rigidly classified nor the different classes accurately defined, figures in such tables are only approximately correct. Moreover, the loss in the different processes will vary with the efficiency of the machines employed. Thus, if the dusting is very thorough, the loss in this process will naturally be heavy, while the loss in boiling and breaking will be correspondingly less. New rags occasionally contain a large proportion of mineral matter and starchy substances in the form of dressing. These substances should be removed before boiling as the alkaline liquors do not readily dissolve the starch but convert it into gelatinous substances which may give trouble in the treatment at later stages. The removal of the starch may be effected by boiling the rags in water and then lowering the temperature to 60° C. and adding a malt extract preparation which has the power of hydrolysing the starch and converting it into water soluble products (sugars) which can be subsequently washed out. But new cuttings can be put into the breaker without previous boiling.

The following data in respect of rags will give a general idea of the loss on conversion into half-stuff.

Moisture.—Under normal circumstances this will vary from 3 per cent. to 8 per cent.; new pieces containing least, while cotton rags generally contain less than linen. Beadle found 7·4 per cent. as the average of several different qualities of rags. The following table gives the amount of moisture contained in some of the vegetable fibres in the air-dried condition and also the maximum amount they will take up (Matthews) :—

TABLE XXIV.

MOISTURE IN VEGETABLE FIBRES.

Fibre.	Air-dry Condition.	Maximum Amount Hygroscopic Water.
Cotton	6·66	20·99
Flax	4·20 to 5·70	13·90 to 24
Jute	6·00	23·30
China grass	6·52	18·15
Manila hemp	12·50	40·00
Sunn hemp	5·31	10·87
Esparto	6·95	13·32
Ramie	6·52	18·15

It is quite possible to sprinkle rags with water before making up into bales, in order to increase the weight. If this were judiciously done, the water would gradually permeate and diffuse evenly throughout the mass. If the rags have a damp feel and excess of water is suspected, a pound or two taken from different parts of the bale should be weighed and then dried, and after drying immediately weighed again, the loss in weight will be due to moisture. (For details as to carrying out the drying process, see *Determination of Moisture in Wood Pulp.*)

Loss on Conversion to Half-stuff.—The loss on sorting and cutting will probably not exceed 2 or 3 per cent., but the loss on dusting, if this be efficiently carried out, may be considerable. The following figures are commonly quoted for the total loss up to the dusting stage when the rags are ready for boiling, but qualities vary so much that it is difficult to give definite figures :—

TABLE XXV.

LOSS ON CUTTING AND DUSTING RAGS.

	Per Cent.
White, fine and medium	6-9
,, coarse	10-15
Cotton, white	6-10
,, coloured	10-13
Coarse materials and bagging	15-20

The loss on boiling may vary within wide limits and depends a good deal on previous treatment ; 5 to 15 per cent. will be about the average, although some of the coarsest rags and new unbleached cotton may lose 20 per cent. or more. The loss in breaking and bleaching will vary considerably, being again dependent on the previous treatment. Five to ten per cent. may be taken as about the average. The total loss in making half-stuff from rags will not vary so much as might be expected from the above figures, as a heavy loss in one stage of the process is often compensated for by a comparatively small loss in another. The total loss will be seldom less than 12 per cent., and will not usually exceed 35 per cent., or, in other words, the yield of bleached fibre will probably exceed 65 per cent., but will only in a few cases exceed 88 per cent. On this basis 70 per cent. may be taken as a fair average yield of half-stuff. In one instance where a calculation of yield was made I found only 50 per cent. approx. The estimation of loss on treatment can be got at by practical tests on a small scale of the moisture, ash, and loss on boiling and washing.

TABLE XXVI.

Loss on Boiling and Bleaching Rags (Beadle).

	Loss on Boiling per Cent.	Loss on Bleaching.	Loss on Boiling and Bleaching.
Best new cotton pieces	8·71	3·29	12·0
Low ,, ,,	12·2	7·7	19·9
Cotton rags, No. 1	5·8	6·2	12·0
,, ,, 2	7·0	6·9	13·9
,, ,, 3	12·5	4·3	16·8
,, ,, 4	13·3	13·7	27·0
New unbleached cotton	23·5	13·0	36·5

Ash.—In a good class of clean rags the ash will not generally exceed 2 or 3 per cent., but dirty rags may contain a considerable quantity. As much as 2½ per cent. of sand may be removed in sorting and dusting. Sometimes new cuttings are very heavily loaded with mineral matter and starchy substances which have been added in the process of "dressing." Beadle states that he has known such rags to yield as much as 60 per cent. of ash, as with plaster cloth, etc. To determine the ash a fair sample of the rags must be selected; this may be done by cutting little bits off a large number of pieces, weighing and burning to ash in the ordinary manner.

Iron in Rags.—Rags may contain a considerable proportion of iron, most of which is removed in the rag dust. For purposes of testing the iron may be extracted either from the rags or from the ash by digesting with dilute hydrochloric acid which dissolves out the iron; the solution is then tested colorimetrically, as described under WATER. The accompanying table gives the percentage of iron per 100,000 parts of material. It will be seen that the fibrous material contains very little iron when new and clean, but that larger quantities are taken up when the material is subjected to wear and tear.

TABLE XXVII.

IRON IN RAGS (BEADLE).

	Parts of Iron per Hundred Thousand.
Cotton wool	6·0
New pieces	1·0
Unbleached cotton	14·0
New canvas	18·0
Rag dust	175·0
Dirty rags	65·0
Clean ,,	25·0

Yield of Fibre.—For this purpose methods can be employed which are generally applicable to all raw fibrous materials. These will now be described as applied to rags.

Experimental Boiling with Alkalies.—For this purpose a fair sample is treated with an alkaline liquor on the same lines as in practice, either (1) The sample of rags is tied up in a stout cloth and thrown into the boiler with the rest of the charge; the cloth should be of open texture, such as cheese-cloth, so as to permit the passage of the alkaline liquid through the rags; on the other hand, it must be sufficiently strong to stand the treatment without going to pieces. When the contents of the boiler are discharged the bundle is picked out from the rags and treated further, as below. (2) The rags are boiled in a small experimental boiler, holding at least a couple of quarts. If possible, the boiler should rotate. A weighed quantity of rags is put into the boiler with the proper proportion of alkali, and the boil is carried on under the same conditions as in practice in respect to temperature, pressure, etc. The employment of an experimental boiler has this advantage over the method described in (1), namely, that the conditions of the boil can be varied at will and the amount of alkali used up can be estimated. (3) There is a third method which is not so applicable to rags as to other raw fibrous materials. It consists in removing dirt and other foreign matter by chemical processes without having resource to boiling under pressure. When it is desired to test a sample of rags and neither process—(1) nor (2)—is applicable, the rags may be boiled with alkali in an open vessel. In this case, however, a larger proportion of alkali will be necessary. After boiling, the rags are washed by placing them in a cage of wire-gauze, and allowing a stream of water to flow through them. They are then pressed, dried and weighed.

Examination of Rag Liquors.—In carrying out the above experimental tests the rag liquors should be examined after boiling, in order to determine what proportion of alkali has been used in the operation. The same applies when controlling rag boiling on a large scale. By these tests the use of too large an excess of alkali is avoided, and the boil is not prolonged more than is necessary. To prolong the boil after the alkali has done its work is to waste time and steam, and possibly to damage the fibre as well. Taking a case where soda is used for boiling, the liquor and washings are made up to a definite volume, say one liter and a convenient quantity, say 50 c.c., is evaporated to dryness in a platinum dish. The dish and contents are then ignited till the whole of the organic matter is burnt off and the ash is white or grey in colour without any black particles. To accelerate this process the dish is allowed to cool from time to time, moistened with water, dried and re-ignited. When the ignition is complete the dish is allowed to cool and immediately weighed. On subtracting the weight of the dish the total amount of soda (Na_2CO_3) in the original liquor may be calculated by multiplying by $\frac{1000}{50} = 20$. As a further check, the contents of the dish are dissolved out by repeated treatments with water, and the alkaline liquor titrated with decinormal acid with methyl orange as an indicator. As each c.c. $\frac{N}{10}$ acid is equivalent to ·0053 gram Na_2CO_3, the total amount of the soda in the original liquor before boiling will be given by multiplying the number of c.c. required by $\frac{1000}{50} \times {\cdot}0053 = {\cdot}106$.

To determine the amount of alkali remaining in the liquor another 50 c.c. are taken and titrated with decinormal acid. Owing to the dark colour of the liquor it is useless attempting to add an indicator direct, but a drop of the liquid is placed upon a piece of sized red litmus paper from time to time, and the addition of acid continued until the liquor no longer produces a distinct blue stain. From the amount of acid required the amount of free alkali may be calculated as above. Of course if the result is required in terms of $NaOH$ or Na_2O, the factors in the calculation will be ·004 and ·0031 respectively, instead of ·0053. The rate at which the alkaline liquor is used up in the course of rag-boiling can be accurately followed by withdrawing small quantities of liquor from time to time, and testing in this manner. It must not, however, be forgotten that, as steam is constantly being condensed in the boiler during the whole boiling, the liquor becomes gradually more and more dilute, and it is advisable to determine both free and total alkali, and express the proportion of free alkali as a ratio.

Table XXVIII. gives a number of tests made on these lines.

Choice of Alkali for Rag-Boiling.—Rags may be boiled with :—

(1) Lime.

(2) Lime and sodium carbonate (soda ash) or the latter alone.

(3) Caustic soda.

In the case of (2) and (3) the final result is the same, as the lime in dilute solution acts on sodium carbonate to produce calcium carbonate and caustic soda, the caustic soda liberated then acts upon the rags. In England lime in conjunction with sodium carbonate or caustic soda are usually employed, while on the Continent and in America lime alone is frequently used. The relative advantages of lime and soda may be summed up as follows :—

Excess of lime is useless but harmless in the boiler, while excess of soda may have an action on the fibre.

Lime soaps formed by the decomposition of greasy and fatty substances are insoluble, while soda soaps are soluble.

TABLE XXVIII.

EXAMINATION OF RAG LIQUORS DURING DIFFERENT STAGES OF BOILING (BEADLE).

Quality of Rags.	Weight of Charge in Cwt.	Gallons of Liquor per Cwt.	Strength of Cold Liquor per Cent. Na_2O.	Percentage of Na_2O on Rags.	Free Na_2O at Different Stages of Boiling when Total Na_2O = 100.					
						1 hour.	2 hours.	3 hours.	4 hours.	5 hours.
No. 1 and 2 cottons (mixed)	—	—	—	—	100	72	48	18	—	—
,, ,, ,, ,,	32	24·0	0·33	0·697	100	38	15	8	—	—
No. 2 cotton	—	25·7	0·654	1·68	100	48	24	19	—	—
No. 3 ,,	—	22·0	0·90	1·78	100	60	27	17	—	—
,, ,,	—	24·0	0·70	1·50	100	49	31	17	—	—
,, ,,	—	25·2	0·55	1·22	100	70	43	13	10	—
,, ,,	31	24·0	0·65	1·36	100	31	21	15	—	—
,, ,,	30	25·5	0·76	1·74	100	43	30	25	—	—
No. 3 and 4 cottons (mixed)	—	25·0	0·80	1·74	100	69	43	26	23	—
No. 2 linen	32	24·0	1·17	2·45	100	25	20	19	—	—
No. 3 ,,	—	23·0	1·44	—	100	40	24	17	13	13
No. 2 and 3 linen (mixed)	32	24·0	0·91	1·91	100	80	24	9	7	—
No. 3 linen	32	24·0	1·0	2·14	100	50	20	15	11	—
No. 4 ,,	—	25·5	1·36	—	100	29	16	15	11	—
Cotton waste (hulls)	—	28·0	1·76	4·40	100	32	28	24	22	21

Lime is said to have a less destructive action on the fibre than soda.

Lime is cheaper than soda, but a larger quantity and higher pressure is required.

Lime is only slightly soluble in water, so that when boiling with lime alone it is necessary to bring it frequently in contact with fresh portions of water by using revolving boilers and keeping the rags in motion.

In a boiling with caustic soda stationary boilers can be used.

Some colours in rags are destroyed by soda but not by lime.

TABLE XXIX.

General Data for Rag-Boiling.

	When boiling with		
	Lime. Continental Practice.	Lime. American Practice.	Soda.
Pressure . . .	40-50 lb.	60-80 lb.	15-30 lb.
Length of boil . .	8-15 hours.	12-18 hours.	3-7 hours.
Proportion of chemical	9-14 °/ₒ.	5-18 °/ₒ.	5-8 °/ₒ.

The accompanying table gives typical instances of the amount of lime and time of boil when treating rags :—

TABLE XXX.

Data for Rag-Boiling with Lime.

Per 100 Lb. of Rags.	Lime. Lb.	Length of Boil. Hours.
White linen . . .	8·3-9·4	8
,, ,, (outshots) .	8·3	8
Cotton rags . . .	9·3	8
,, ,, (seconds .	11·2	9
,, ,, (greys) . .	10·11	10
,, ,, (outshots) .	10	10
Mail bags . . .	11	11-12
Blue linens . . .	12-13·7	10
,, ,, (outshots) .	12·3	10
Woollen rags . . .	16	12

The advantage of boiling under pressure does not depend on any peculiar action of the pressure, but on the fact that it allows the temperature to be raised above the normal boiling point of the liquor. The accompanying table gives the corresponding pressure and temperatures of water when heated above the normal boiling point. The figures do not apply exactly to an alkaline liquor as the presence of the alkali raises the boiling point.

TABLE XXXI.

TEMPERATURES CORRESPONDING TO PRESSURES IN BOILERS.

Registered Pressure. Lb. per Sq. In.	Temperature. Degrees Far.	Registered Pressure. Lb. per Sq. In.	Temperature. Degrees Far.
0	212	55	302·6
5	227·2	60	307·2
10	239·4	65	311·7
15	249·8	70	315·9
20	258·8	75	320·0
25	266·8	80	323·8
30	274·0	85	327·6
35	280·6	90	331·1
40	286·7	95	334·4
45	292·4	100	337·8
50	297·6		

(CALCULATED FROM ANOTHER SOURCE.)

Temperature. Degrees Centigrade.	Lb. per Sq. In.
100	0
105	2·82
110	6·08
115	9·82
120	14·10
125	19·00
130	24·50
135	30·80
140	37·80
145	45·05

In some cases small quantities of volatile gases, such as ammonia, are produced in the process of boiling.

Rag boilers are usually spherical, and 8 feet to 12 feet in diameter. The thickness of the plate will vary with the size; for the smaller sizes ½ inch is usually regarded as sufficient, for larger sizes ⅝ inch. The tendency at present is to make the boiler of thicker plate and to work with a higher pressure, although it is doubtful if any advantage is gained by allowing the pressure to exceed 30 lb. per square inch.

Spherical boilers are usually preferred, as for a given thickness of plate the weight is less, the area of surface is less, and therefore loss of heat by radiation is less, while the cubical content is greater than for boilers of any other form.

Wood Pulp Raw Material.—Wood for converting into pulp is obtained chiefly from coniferous trees such as pine, fir and spruce. In addition some of the softer woods, such as poplar and aspen, are used; these, however, yield a shorter-fibred pulp. Wood is measured in English-speaking countries by the "cord," representing 128 cubic feet of piled wood; that is to say, 4-feet lengths stacked up to measure 4 × 4 × 8. Griffin and Little found the weight of one cord of green spruce (37 per cent. moisture) to be 4440 lb. The figures recently given by De Cew are to be found in Table XXXIX. According to these a cord of spruce may be taken as weighing about one ton. On the Continent wood is measured by the cubic meter = 35·3 cubic feet of piled wood. One cubic meter of air-dry wood (spruce) may be reckoned as weighing about 370 kg. Of the total volume occupied by piled wood about ¼ may be reckoned as air space, or more accurately 1 cubic meter = ·77 cubic meter of solid wood. 100 kg. air-dry wood occupy ·21 cubic meter (without air spaces, *i.e.* solid). Different figures will be obtained for different woods. 100 kg. may occupy as much as ·35 cubic meter (solid).

For pulp-making it is sometimes necessary to distinguish between the heart wood and sap wood; the former consists of the centre portion of the trunk, the fibres of which have ceased to grow. The sap wood is the wood of more recent growth and contains a larger proportion of albuminous and easily decomposable organic matter, while the heart wood is more durable. The growth of a tree depends on the formation of cells on the inner side of the cambium. The cambium forms a layer just inside the bark, or more correctly cortex, and consists of the living part of the trunk from which all growth springs. The rings of recent growth inside the cambium form the sap wood, and as each year a fresh ring of sap wood is formed the innermost ring of sap wood changes into heart wood.

The composition of woods, especially as regards moisture, varies considerably with the time of year. Some of the more important properties of American pulp wood, such as specific gravity and ash, are given in the accompanying table :—

TABLE XXXII.

SPECIFIC GRAVITY AND ASH OF AMERICAN PULP WOODS (SHARPLES).

Botanical Name.	Common Name.	Specific Gravity.	Weight of Cubic Foot in Lb.	Ash per Cent.
Pinus strobus	White pine	0·3485	21·72	0·12
Pinus Banksiana	Grey pine of Canada	0·4761	29·67	0·23
Picea nigra	Spruce	0·4087	25·47	0·30
Abies grandis	Fir	0·3545	21·97	0·49
Abies Fraseri	Balsam	0·3565	22·22	0·54
Larix Americana	Tamarack	0·7024	43·77	0·27
Populus grandidentata	Poplar	0·4632	28·87	0·45
Populus tremuloides	Aspen	0·3785	23·59	0·74
Populus monilifera	Cottonwood	0·4494	28·00	0·65
Salix nigra	Willow	0·4456	27·77	0·70
Fagus ferruginea	Beech	0·7175	44·71	0·54
Acer dasycarpum	Maple	0·5269	32·84	0·33
Betula alba	White birch	0·6160	38·05	0·29
Betula papyrifera	Paper birch	0·6297	39·24	0·23
Æsculus glabra	Buckeye	0·4542	28·31	0·86
Liquidambar styraciflua	Sweet gum	0·5615	34·99	0·48
Taxidium distichum	Cypress	0·4084	24·45	0·40
Tanga Canadensis	Hemlock	0·4097	25·53	0·48
Castanea vulgaris	Chestnut	0·4621	28·80	0·13
Tilia Americana	Basswood	0·4525	28·20	0·55
Robinia pseudacacia	Locust	0·7257	45·22	0·23

From the point of view of the pulp-maker, the more important constituents of wood consist of mineral matter, resin and moisture, in addition to cellulose and incrusting matter. The percentage of mineral matter in the form of ash is given in Sharples' table. The percentage of resin in wood has been studied by Ulbricht, whose results are given in the accompanying table :—

TABLE XXXIII.

PARTS OF RESIN PER 100 PARTS OF WOOD (ABIES EXCELSA).

	Sap Wood.	Heart Wood.	Entire Wood.
Winter	1·966	2·299	2·213
Spring	1·781	2·041	1·911
Summer	1·987	2·235	2·109
Autumn	2·024	2·158	2·137

The figures were obtained by extracting the wood with alcohol, so that everything soluble in alcohol is reckoned as resin. Resin is readily acted upon and saponified by alkaline liquids, so that where the wood is treated with alkalies, as in the soda and sulphate processes, the percentage of resin is only of secondary importance. Resin, however, influences the properties of mechanical pulp, and also sulphite pulp, as the acid sulphite liquors have but little action on resinous substances. As will be shown later, sulphite pulp invariably contains a much larger proportion of resin than soda pulp. The quality of the pulp will also be affected by the distribution of the resin, that is to say, whether it is evenly distributed throughout the mass or localised at certain points.

Not only does alcohol extract substances from wood, but other solvents, such as water, remove some of its constituents, such as tannin, gums, mucilage, sugars and other carbohydrates. The accompanying table gives the extract on treating wood successively with water, ether, and alcohol:—

TABLE XXXIV.

EXTRACTION OF WOOD WITH DIFFERENT SOLVENTS (GRIFFIN AND LITTLE).

	Water—Removes Gums, Mucilage, Sugars, Tannin, etc.	Ether.	Alcohol.	Total Removed by Ether and Alcohol includes Resins, Oils, Waxes.
Spruce . .	4·83	1·67	1·61	3·28
Poplar . .	4·80	0·85	1·00	1·85
Cottonwood .	4·69	0·79	2·04	2·83
Sweet gum .	3·39	0·30	0·55	0·85
Beech . .	2·14	0·38	0·55	0·93
Yellow birch .	1·88	0·32	0·65	0·97
Cypress . .	4·22	0·81	0·94	1·75

Finally, there is the question of moisture. Coniferous trees in general contain a larger proportion of moisture (50 to 60 per cent.) than the hard wood (deciduous) trees (say 40 per cent.). As a rule spruce contains less moisture than Scotch fir. However, Griffin and Little found only 37 per cent. of moisture in a quantity of green spruce they examined. Gelesnoff made a number of determinations of water in entire trees, with the following results :—

TABLE XXXV.

Moisture in Wood.

	Minimum.	Maximum.	Average.
Scotch fir . . .	55·3	64·0	61·1
Aspen . . .	48·9	56·6	52·8
Birch . . .	43·5	65·9	49·2

Elaborate analyses were also made by Ziegelmeyer (see Chemical Pulp).

Mechanical Wood Pulp.—Mechanical pulp is prepared by grinding logs of wood against the periphery of a large grindstone. The wood is first barked, either by hand or machine.

(1) *By Hand.*—The bark is stripped from the logs by means of a knife provided with two handles, something like a spokeshave. In Germany a good workman can bark four cubic meters of medium-sized logs in one day (10 hours).

(2) *By Machine.*—In the ordinary barking machine the log is held against angle knives projecting through slots in a revolving disc, the action being somewhat similar to that of an ordinary plane, the disc making 300 or 400 revolutions in a minute. After treatment in the machine it is often necessary to go over the logs again by hand, especially when the logs are not quite straight, in order to remove pieces of bark which have escaped the action of the machine. In some works, especially in districts where wood is comparatively cheap, it is the custom when cutting up the logs to throw out crooked pieces. Schubert has worked out the relative cost of barking by hand and machine. Wood barked by machine and afterwards gone over by hand costs 5½ marks per 10 cubic meters (solid), while the cost of barking the same quantity by hand alone is 10 marks. In the latter case, however, the loss

on barking is 1·4 per cent. less. In America another system is in vogue, in which the logs of wood are thrown into a revolving drum or tumbler containing water, the friction of the logs against one another removes the bark. The logs are then taken to the grinders. These are of sandstone, the grinding surface being ½ to 1 meter broad. They are "sharpened" by going over the grinding surface with a tool and covering it with small indentations or burrs. The stone is fitted with presses, consisting of boxes or "pockets," into which the logs are placed and forced against the surface of the stone by hydraulic pressure. The logs are usually placed parallel to the axis of the stone. Water is allowed to flow on to the surface of the stone during the grinding, carrying away with it the particles of fibre torn off by the stone. The amount of water may be 400 or 500 times that of the pulp (cold grinding) or only some 30 to 50 times (hot grinding). In the latter case a greater pressure can be applied and the lower part of the stone dips into water. Machines of this type are usually constructed with fewer pockets; they are also said to produce a larger quantity of pulp for the power expended. The pressure exerted by the wood on the face of the stone varies considerably, but may be taken as about 10 kilos. per sq. cm., or 140 lb. per sq. inch. The stone makes about 250 revolutions per minute.

Cold grinding is still very generally used on the Continent, hot grinding in America. For rough purposes of reckoning 1 h.p. is required for every 500 grams air-dry pulp per hour. Machines of good German make require 7 to 8 h.p. to grind 100 kg. in 24 hours. Under the most favourable circumstances the power required may be reduced to 6 h.p., but when it is desired to produce the finest pulp as much as 9 or 10 h.p. is necessary; in other words, 1 h.p. under the most favourable circumstances will produce about 700 grams of pulp per hour.

In large machines of modern make the grinder is driven from the same shaft as the motor, thus effecting a saving in transmitting power. In addition to the grinder there are other machines, termed refiners, consisting of two stones, the axis being vertical: the lower one is fixed, the upper one revolves. The pulp from the grinders passes through a hole in the upper stone, and then between the two stones, finding its way out at the periphery; it then passes to a sorting machine with oscillating sieves. The more modern machines are constructed on the centrifugal principle. The older form of machine consists of three shaking, flat sieves situated over one another, with mesh 3·5-3·6 mm., 1·5-1·8 mm., ·6-1 mm. respectively. A machine with sieves 1·2 m. long and ·48 meters broad will treat stuff to produce 600 kg. air-dry pulp in 24 hours. In America, instead of sieves, plates with slits similar to strainer plates are used; width of slit, ·28-·38 mm. The power required to produce mechanical pulp, by machines working on the principle of cold and hot grinding respectively, has been worked out by Kirschner.[1] The figures are as follows (a comparison is made between plants taking 150 h.p.):—

TABLE XXXVI.

COMPARATIVE TRIALS ON PRODUCTION OF PULP BY COLD AND HOT GRINDING (KIRSCHNER).

GRINDING REQUIRING 150 H.P.

Cold.

Heavier gearing 30 °/o	45 H.P.	
1 refiner working twenty-four hours	15 ,,	
2 sorting machines	5 ,,	
1 board machine	3 ,,	
Raising water for grinder	2 ,,	
		70 H.P.
There remains for grinding with two five-press machines		80 ,,
		150 H.P.

Output in twenty-four hours 2000 kg. 100 kg. pulp in twenty-four hours require 7½ h.p. 1 h.p. produces 556 grams.

Quite recently some very complete experiments have been carried out with grinding of wood pulp by the Forest Products Department of the United States Department of Agriculture (Bulletin No. 343, published in 1916). This work comprises experiments made with a full-size grinder arranged for variable speed. The raw material was spruce wood which was used either untreated or with previous boiling or steaming. As regards the relative effect of hot and cold grinding, the authors (J. H. Thickens and G. C. McNaughton) remark that although it is true

---

[1] See Kirschner, *Wochenblatt*, 1910, **41**, p. 1995. Abstract, *Soc. Chem. Ind.*, 1910, p. 873.

that the output is less when grinding cold, the variation is not great. "The pulp is somewhat finer when ground cold, but there is not as much difference between pulps manufactured by the cold and hot processes as is generally believed."

It is not possible within the space at my disposal to deal in detail with the results of the numerous experiments, but I give the authors' summary of their results as applied to cooked wood, that is wood which has previously been treated with hot water or steam, and the uncooked, that is untreated wood.

"COOKED WOOD.

"1. Cooking spruce prior to grinding results in a stronger fibred pulp, although at least 25 per cent. more power per ton is required than is used in grinding untreated wood. The horse-power consumption per ton when grinding under conditions of varying cylinder pressure decreases to a minimum at approximately 65 lb. pressure on a 14 inch cylinder; this holds for dull or sharp stones.

"2. When wood is cooked under conditions of constant pressure and varying lengths of time, the maximum power consumption per ton of pulp is obtained after cooking for six hours. This holds true regardless of the pressure at which the cooking takes place, between 0 and 75 lb. gauge pressure.

"3. Wood which is cooked at high pressure requires more power per ton of pulp when ground under the same conditions of cylinder pressure, speed and surface of stone than wood which is cooked at lower pressure, if the duration of the cook is the same. Likewise, the production of pulp in 24 hours is materially less when the wood ground has been cooked at high pressure, than if it had been cooked at low pressure.

"4. The yield per cord is influenced very greatly by the length of time the cooking is carried on and the pressure of the cook, being much lower for high pressures than for low, and also for long cooking periods than for short.

"5. The power to the grinder increases with speed and pressure of grinding and decreases with the degree of sharpness of stone. There is also a very slight increase in the power required with increase of temperature, other conditions remaining constant, while the thickness of stock in the grinder pit has almost no influence. Under like conditions of all other factors the power to the grinder is less for steamed wood than for green or seasoned wood untreated.

"6. With a fixed amount of power to the grinder and a fixed grinding pressure, the speed of the pulp stone will vary greatly, depending on the length of time the wood has been steamed and the steaming pressure. Unsteamed wood will grind at low speed, while that steamed a long time will grind at high speed with the same amount of power to the grinder.

"7. There is little if any difference in the quality of pulp obtained as a result of using either the boiling or steaming process. The colour, length of fibre, and yield are practically the same if the boiling or steaming is carried on at the same temperature.

"8. The amount of pulp produced in grinding cooked wood with a fixed amount of power to the grinder is less at high pressure and low speed than it is at low pressure and high speed. This results in a greater horse-power consumption per ton of pulp at high pressure and low speed."

"UNCOOKED WOOD.

"1. The rate of production varies directly with pressure, speed, and degree of sharpness of stone. Less pulp is obtained in 24 hours using seasoned wood than with green, and still less using steamed wood, all other conditions being the same. The temperature influences the rate of production to some extent; less pulp is produced at low temperatures.

"2. The horse-power consumption per ton of pulp when untreated wood is ground increases as the pressure decreases according to a fairly definite law; it is lower on sharp stones than on dull ones, and increases as the speed decreases in much the same manner as it does with pressure. There is, however, not as much difference between the power consumption per ton at low speed and high speed as there is between power consumption at low pressure and high pressure. The power consumption is very little influenced by temperature, but it is slightly lower at high temperature. The power consumption is higher for seasoned wood than for green wood, and higher for steamed wood than for either seasoned or green material ground under the same conditions.

"3. The yield of pulp per cord is greater at high pressure than at low, and, while this is true also of the screenings, there is not as much fine material lost in white water when high pressure is used. The yield is not greatly influenced by the surface of the stone, but is slightly higher at high speed than at low. The yield is proportional to the bone-dry weight per cubic foot of wood.

"4. The quality of pulp varies greatly with the surface of the stone, less with the pressure, and least with the speed. The weight per cubic foot and character of wood influence quality to a marked extent, especially the latter; temperature also has a marked influence; pulp of greater strength is obtained at higher temperature; pulp produced at low temperature will take a better finish. Pulp of better colour can be obtained from green wood than from seasoned, and stronger pulp can be obtained by cooking the wood prior to grinding. The quality of paper manufactured under exactly the same conditions, but made of pulp produced at different grinder pressures, varies greatly with the grinder pressure and the horse-power consumption per ton of pulp. Mechanical pulp of greatest strength can be produced only by the expenditure of a relatively large amount of power."

The same authors have also investigated the suitability for mechanical pulp of 24 woods which grow in quantity in the United States of America. Full tabular details are given of the result of the experiments, and the pulp produced was tested not only by conversion into paper on a manufacturing scale but the paper was subsequently used for whole editions of newspapers, so that the woods were given a very practical test. The suitability was of course found to vary; some woods yield a dark pulp which is not suitable for newspapers, but could be used very well for wood pulp boards. These woods include, Jack pine, Tamarack, Loblolly pine, and Larch. Of the woods tested which produced a relatively light-coloured pulp may be mentioned Alpine fir, Engelmann spruce, Lowland fir, Lodgepole pine, Balsam fir, White fir, Amabilis fir, Noble fir, Sitka spruce, Western hemlock and Eastern hemlock.

The tendency in America appears to be to use greater power on the grinders; 600-750 h.p. is frequently employed and in the case of automatic magazine grinders 1000-1200 h.p.

Yield of Mechanical Pulp.—The following data represent Kirschner's most recent calculations and apply to German spruce:—

1 cubic meter wood with bark yields ·669 solid cubic meter, yields 234 kg. air-dry pulp.

1 cubic meter wood with bark yields ·87 cubic meter of barked wood.

1 cubic meter barked wood yields $\frac{\cdot 669}{\cdot 87} = \cdot 769$ solid cubic meter, yields 269·2 kg. air-dry pulp.

1 solid cubic meter barked wood weighs 480 kg. and yields 350 kg. air-dry pulp.

The loss on the wood by conversion into mechanical pulp therefore amounts to 27 per cent. by weight.

These figures do not take into consideration any fibre recovered on a Fullner filter or other contrivance, by which 5 to 8 per cent. may be recovered, thus reducing the loss, under favourable circumstances, to 19 per cent. The loss will also depend on the method of grinding; thus by different methods of grinding a close-grained wood weighing when barked 389 kg., the cubic meter gave in one case 312 kg. air-dry pulp, equivalent to a loss of 19·8 per cent.; in another case, 298 kg. air-dry pulp, equivalent to a loss of 23·4 per cent.; leaving out of account any fibre recovered on filters.

Tauss made a number of experiments, boiling beech wood and pine wood with caustic soda of various strengths. The results as calculated by Surface are given in the following table:—

TABLE XXXVII.

EXPERIMENTAL BOILINGS OF BEECH AND PINE WOOD WITH VARYING CONCENTRATIONS OF CAUSTIC SODA.

Material.	Strength of NaOH Solution. Grams per Liter.	Residues from Boiling. Pressure, Pounds per Square Inch.										
		0.					58·8.			132·3.		
		(1 Atmosphere.)					(5 Atmospheres).			(10 Atmospheres.)		
		1	2	3	4	5	1	2	3	1	2	3
Pure cellulose (Swedish filter paper)	140	7812					2267					
	80	8301	7814	7721			5548	4624	4198	4971	4320	4102
	30	8793					8464			7972		
	0	10000					9926	9886	9861	9056	8672	8652
Beech wood (fine shavings)	140	5357					852					
	80	5829	4810	4532			3564	3277	3020	2934	2402	2061
	30	6975					4434			3441		
	0	9620	9400	9275			7840	7440	7315	8632	8220	8159
Pine wood (fine shavings)	140	6455					287					
	80	6611	5926	5480	5157	4863	4309	3253	2415	2568	2111	1820
	30	7163					4904			2969		
	0	9882					8460	8153	8082	8822	8510	8390

In explanation of the above table it may be stated that 10 grams air-dry weight of material was treated in each case with 500 c.c. of the liquor. The yields are given taking the original weight = 10,000. The columns 1, 2, 3, etc., represent fresh boils with the same material so that a certain quantity of additional material is removed in each successive boil. It will be noted that appreciable quantities of wood are dissolved by a strength of solution equal to 0, that is to say, by pure water.

H. E. Surface[1] has published a large number of boiling

---

[1] *Bulletin of U.S. Dept. of Agriculture*, No. 80.

trials, using aspen. The strength of the soda, the time of boil and the pressure were varied. The tables are too full to reproduce. The total yield of crude pulp varied from 45-58 per cent. according to the severity of the boiling treatment, and this mainly corresponds to the amount of caustic soda consumed per unit of wood. The microscopic appearance of the fibres was found to be a good guide as to the severity of cooking. As would be expected, Surface also found that less bleach was required the more severe the boiling treatment. The minimum duration of treatment was found to be 3-4 hours, and it was found that aspen could be successfully treated with 20-25 per cent. of caustic soda on the weight of the wood.

CHEMICAL WOOD PULP.—There are three processes for converting wood into chemical pulp—namely, the soda, sulphate, and sulphite processes. The latter of these three accounts for by far the largest proportion of chemical pulp manufactured. Whatever the process employed, the wood is first barked by hand or machine and cut up into convenient lengths. This involves a loss amounting to about 13-28 per cent. In a test made on a cord of green spruce by Griffin and Little the loss amounted to almost 20 per cent. For details see accompanying tables. The wood is then chopped up and filled into the boilers.

Soda Process.—In this process the wood is boiled with caustic soda in the same manner as rags or esparto, but the process in general is carried out under a higher pressure and with a larger proportion of alkali. I give the following figures as an average of general practice :—

TABLE XXXVIII.

GENERAL DATA FOR THE PRODUCTION OF SODA PULP.

Amount of caustic, 12 to 20 °/ₒ (up to 90 °/ₒ of this is recoverable. See Soda recovery).

Strength of caustic liquor, 10 to 14 B. (15 to 22 Tw., that is about 5 to 8 °/ₒ Na_2O).

Pressure, 130 to 160 lb. per square inch, the temperature approaching 360° F. (180° C.).

Length of boil, 6 hours.

The conditions of boiling will, however, vary with the variety of wood, and I append here the figures given by different authorities :—

TABLE XXXIX.

DATA FOR THE PRODUCTION OF SODA PULP.

SCHUBERT.

Strength of caustic . . .	10 B.	12 B.
Pressure, lb. per sq. in. .	132-147	88-118.
Length of boil . . .	6 hours	6 hours.

HENRY E. SURFACE.

	Quantities per Pound of Bone-Dry Wood.				Duration of Boiling.
	Total Liquor Gallons.	NaOH per Cent.	Na_2CO_3 per Cent.	Total Na_2O per Cent.	Hours.
Aspen . . .	·449	28·5	1·0	22·7	7·5
Beech . . .	·369	28·5	1·7	22·9	8·4
Cotton gum . .	·399	29·9	2·2	24·5	8·3
Douglas fir . .	·333	25·0	·7	19·8	7·5
Engelmann spruce .	·407	29·2	1·2	23·2	8·2
Grand fir . . .	·396	29·6	1·9	24·0	8·6
Incense cedar . .	·421	28·7	1·4	23·1	9·2
Jack pine . . .	·333	25·0	·7	19·8	7·5
Loblolly pine . .	·333	25·0	·7	19·8	7·0
Lodgepole pine . .	·389	28·0	1·2	22·4	10·0
Longleaf pine . .	·289	21·7	·6	17·1	7·3
Red alder . . .	·510	34·1	1·6	27·3	6·2
Red maple . . .	·390	26·1	2·0	21·4	9·6
Sycamore . . .	·410	25·9	1·5	22·1	9·3
Tamarack . . .	·366	27·5	·8	21·9	7·0
Tulip tree . . .	·389	26·8	1·7	21·8	9·6
Western hemlock .	·404	26·9	2·2	22·1	9·2
White fir . . .	·346	25·2	·7	19·9	7·0

GRIFFIN AND LITTLE.

Strength of liquor, 8 to 15 B., according to time of boil and pressure. The strength ordinarily used, 12 to 14 B. For poplar, maple, cottonwood, 11 B; and for spruce, pine, hemlock, 15 B.

700 gallons of liquor are required per cord of wood (without making allowance for condensed steam).

Pressure, 90 to 110 lb. per sq. inch.

TABLE XXXIX. (*continued*).

ERNST MÜLLER.

Strength of liquor	12-14 B.
Pressure, lb. per sq. in.	73-147.
Length of boil	5-6 hours.

KLEMM.

Strength of liquor	10-14 B.
Pressure, lb. per sq. in.	73-176.
Length of boil	5-6 hours.

DE CEW.

	Soda as Carbonate.	Sp. Gr.	Weight per Cord.	Yield.	
				Per Cent.	Air-Dry.
	lb.		lb.		
Picea Nigra (Black spruce)	900	0·41	2250	40	1000
Tanga Canadensis (Hemlock)	950	0·42	2300	38	970
Populus grandidentata (Poplar)	800	0·43	2350	44	1150
Tilia Americana (Basswood)	800	0·425	2325	44	1135
Betula alba (White birch)	800	0·58	3190	42	1490
Acer rubrum (Soft maple)	850	0·64	3520	40	1560
Betula lutea (Yellow birch)	850	0·66	3630	40	1610

The boilers may be—

(1) Upright digesters, 15 ft. to 30 ft. high and 4 ft. to 6 ft. in diameter. A common size is 16 ft. high by 5 ft. in diameter.

(2) Large-size spherical rotaries. A 12-ft. rotary will take 5 cords of wood.

(3) Cylindrical rotaries. A boiler 22 ft. long and 7 ft. diameter will take 3 cords of wood.

TABLE XL.

Loss on Treatment and Yield of Pulp.

(Analysis of Woods by Hugo Müller.)

Kind of Wood.	Water.	Substances soluble in Water.	Fat, Wax, and Resin.	Encrusting Substances.	Cellulose.
Scotch fir (*Pinus sylvestris* . . .	12·87	4·05	1·63	28·18	53·27
Fir (*Pinus abies*) .	13·87	1·26	0·97	26·91	56·99
Poplar . . .	12·10	2·88	1·37	20·88	62·77
Birch . . .	12·48	2·65	1·14	28·21	55·52
Lime tree (Linden) .	10·10	3·56	3·93	29·32	53·09
Willow . . .	11·66	2·65	1·23	28·74	55·72
Beech . . .	12·57	2·41	0·41	39·14	45·47

The yields of cellulose given in this table are much higher than those obtained in manufacturing processes, as the percentage of moisture in the wood is greater than that in air-dried pulp obtained from it. Compare De Cew's figures in Table XXXVIII. which are based on actual mill experience.

Ziegelmeyer, the manager of a cellulose mill, made a number of tests in 1890 on the yield of cellulose by the soda process. His figures are given in the table on opposite page.

Max Müller, after many years' experience, arrived at the following conclusions, which are in general agreement with the figures given in Ziegelmeyer's tables :—

1 cubic meter Scotch fir (*Pinus sylvestris*) yielded 104·7 kg. to 108·5 kg. cellulose.

1 cubic meter fir (*Pinus abies*) yielded 94·5 kg. to 100·2 kg. cellulose.

TABLE XLI.

CONSTITUENTS OF WOOD (ZIEGELMEYER.)*

1 cubic meter of recently felled wood gave yields in kg.

Variety of Wood.	Weight with Bark.	† Loss in Barking.	Loss by Drying at 100° C.	Yield of Cellulose Bone-Dry.	Yield of Cellulose Air-Dry 9·09 °/° Water.	Yield Air-Dry Cellulose °/° reckoned on		Yield of Cellulose Dried at 100° C. on Dried Barked Wood.
						Unbarked Wood.	Barked Wood.	
Spruce (*Pinus picea*)	617·5	80	230	108·2	119	19·3	22·2	35
Fir (*Pinus abies*)	757·5	203·5	293·6	96·3	106	14·1	19·1	37
Scotch fir (*Pinus sylvestris*)	697·5	170	252·2	105·2	116	16·6	22·2	38
Stone pine (*Pinus austriaca*)	707·5	147	285·6	86·9	95·6	13·5	17·0	32
Larch (*Pinus larix*)	597·5	90	160·4	116·8	128	21·5	25·2	34
Pine (*Pinus pumilis*)	449·3	55·1	128·4	99·8	110	24·5	27·9	38
Beech (*Fagus sylvatica*)	865	70	327·5	139·8	154	17·8	19·4	30
Birch (*Betula alba*)	623·5	111·5	215·0	85·6	94·2	15·8	18·4	29
Aspen (*Populus tremula*)	695	135	227·4	108·4	119	17·1	21·3	33
Poplar (*Populus alba*)	650	175	226·5	88·1	97·0	14·9	20·4	24
(*Sorbus torminalis*)	756·5	166·5	224·2	104·0	114	15·1	19·3	29
Mountain Ash (*Sorbus aucuparia*)	725·5	131·5	269·7	100·6	111	15·3	18·7	31
Willow (*Salix caprea*)	572·5	80·5	241	85·7	94·3	16·5	19·2	34
(*Salix fragilis*)	583·5	111	181·4	104·8	115	19·7	24·4	36
English Ash (*Fraxinus excelsior*)	593·5	91	100·1	104·0	114	19·2	22·6	26
Alder (*Alnus glutinosa*)	516·5	97·5	181	81·3	94·3	18·3	22·5	34

---

* The yields obtained by Ziegelmeyer appear to be too low.

† For further figures for Loss in Barking, see *Papier Zeitung*, 1909, p. 973.

The cellulose was unbleached and the wood air-dry.

Kirschner made a number of tests, in which blocks of wood were cut into cubes exactly 1 cubic decimeter (10 cm. each way) and then split up into pieces about 40 × 40 × 3 mm. The chippings from each block were placed in a lead box perforated with small holes and boiled along with the rest of the charge in a large boiler. The following yields on air-dried cellulose were obtained from one cubic decimeter of wood :—

TABLE XLII.

Yields of Cellulose from Different Woods (Kirschner).

Variety of Wood.	Grams Air-Dry Cellulose.	Yield per Cent.
Scotch fir (*Pinus sylvestris*)—		
Branches of young wood	150 Grams.	Up to 28
Old wood from the trunk	175 ,,	,, 50
Fir (*Abies excelsa*)—		
Branches of young wood	163 ,,	,, 34·5
Old wood from the trunk	174 ,,	,, 43·5
Fir (*Abies pectinata*)	167 ,,	,, 38
Larch (*Larix europœa*)	195 ,,	,, 35
Weymouth pine (*Pinus strobus*)	130 ,,	,, —
Beech (*Fagus sylvatica*)	250 ,,	,, 34·5
Birch (*Betula alba*)	285 ,,	,, 41·5
Aspen (*Populus tremula*)	208 ,,	,, 33
Poplar, Trunk	127 ,,	,, 33
Branches	152 ,,	,, 33
Lime tree (*Tilia parvifolia*)	146 ,,	,, 31
Willow, Trunk	178 ,,	,, —
Branches	202 ,,	,, —
Oak, Trunk (*Quercus*)	230 ,,	,, 28·7
Elm, Trunk (*Alnus campestris*)	274 ,,	,, —
Alder (*Alnus glutinosa*)	— ,,	,, 30·5
Hornbeam (*Carpilus betulus*)	280 ,,	,, —

TABLE XLII. (*continued*).

PERCENTAGE YIELDS OF SODA PULP AND QUALITY OF PULP FROM DIFFERENT WOODS.

(Average figures from data published by Henry E. Surface.)

(The boiling was carried out in 65 gallon digesters, *i.e.* on a relatively large scale.)

	Yields.	Quality of Pulps.		
	Screened Pulp. Per Cent.	Ash. Per Cent.	Bleach Required. Per Cent.	Loss on Bleaching. Per Cent.
Aspen	50·1	·85	8·1	1·1
Beech	45·2	·79	10·8	1·7
Cotton gum	43·7	1·62	24·9	1·6
Douglas fir	45·7	·1	—	—
Engelmann spruce	40·4	·59	54·3	4·1
Grand fir	43·3	·39	33·5	4·0
Incense cedar	36·3	·84	85·0	9·1
Jack pine	49·9	—	—	—
Loblolly pine	45·4	·0	—	—
Lodgepole pine	40·8	·66	37·7	3·5
Longleaf pine	48·6	—	—	—
Red alder	42·5	·74	21·1	2·9
Red maple	29·1	·77	13·6	2·6
Sycamore	44·4	1·18	14·3	3·2
Tamarack	36·4	—	—	—
Tulip tree	41·1	·95	15·9	2·8
Western hemlock	44·2	—	66·4	—
White fir	49·0	4·7	—	—

Sulphate Process.—In spite of the recovery of soda from the liquors obtained in boiling wood by the soda process, there is a loss which amounts to 8-10 per cent. even with efficient recovery plant. In the sulphate process this loss is made up by the addition of sodium sulphate (Glauber's salts) in the place of caustic soda. In order to add a proportional amount of sulphate 12 to 15 per cent. is required to replace 8 to 10 per cent. of soda. Even with this larger quantity of sulphate a considerable economy is effected, as the price of caustic is much higher than that of sulphate. The principle of the process depends on the fact that in soda recovery when the concentrated liquors are burnt to ash the sodium sulphate reacts with the carbonaceous matter and is thereby reduced to sodium sulphide, while the soda in conjunction with the organic matter is converted into sodium carbonate. The liquors are causticised in the usual manner, the lime converting the carbonate into caustic, but having little action on the sodium sulphide. The operation of boiling is therefore carried out with a mixture of caustic soda, sodium sulphide and unchanged sodium sulphate. The latter has little or no action on the wood. The following analysis gives the proportion in which these substances are contained in the liquor :—

TABLE XLIII.

COMPOSITION OF SULPHATE LIQUOR.

Sodium sulphate	37 per Cent.
Caustic soda	24 ,,
Sodium sulphide	28 ,,
,, carbonate . . .	8 ,,
Other substances	3 ,,

Iron boilers are used, and the conditions of boiling are similar to those in the production of soda pulp. The yield of pulp is rather higher than by the soda process, and the cellulose is said to bleach better with a smaller percentage of bleaching powder.

According to Max Müller, the following figures give the average yield of pulp by the sulphate process :—

1 cubic meter Scotch fir (*Pinus sylvestris*) yielded 113·5-120·4 kg. cellulose.

1 cubic meter fir (*Pinus abies*) yielded 107·3-110·7 kg. cellulose.

The cellulose was unbleached and the wood air-dry.

Compare these figures with those given above for yields of soda pulp by Max Müller.

The wood used for sulphate process is best thoroughly air-dry and well seasoned. The process is also suitable for treating resinous woods. Thus the heart wood of the Scotch fir (*Pinus sylvestris*) is treated by the sulphate process, while the sap wood (wood of recent growth) can be suitably treated by the sulphite process.

Sulphite Process.—The wood for this purpose should be recently felled, as green wood is more easily acted on by the sulphite liquors. In contrast to the foregoing alkaline processes the sulphite is an acid process. The liquors used consist of calcium bisulphite, either alone or in admixture with magnesium bisulphite ($CaH_2(SO_3)_2$ and $MgH_2(SO_3)_2$ containing an excess of sulphurous acid (H_2SO_3). In general, for every 2 parts of sulphurous acid combined as bisulphite the liquor contains 1 part of sulphurous acid in the free state, which latter is known in England and America as free sulphurous acid. On the Continent all sulphurous acid over and above that combined as normal sulphite (Na_2SO_3) is reckoned as free acid, so that by the Continental method of reckoning ordinary sulphite liquors contain about 2 parts free acid to 1 part combined. Griffin and Little propose to call the free acid reckoned on the Continental plan as available acid, and this suggestion is adopted here. The efficiency of the liquors is determined by the proportion of available acid and not by that in combination as sulphite, although, on the other hand, a solution of sulphurous acid in water without the addition of a base does not work efficiently.

There are a number of systems in vogue both for preparing liquor and boiling wood. Sulphur dioxide gas is prepared :—

(1) By burning sulphur.

(2) By roasting pyrites (these contain about half their weight of sulphur).

The gas produced by process 1 is usually stronger than that produced by process 2.

The average strength of gas obtained by burning sulphur = 15 per cent.

The average strength of gas obtained by burning pyrites = 8 per cent., but with the American rotary burners it is stated that as strong a gas can be obtained as by burning sulphur, *viz.* 14-16 per cent. SO_2.

Many plants have been devised for absorbing the sulphur dioxide gas and preparing the sulphite liquor. The absorption plant adopted will depend a good deal on the strength of the liquor it is desired to produce. These plants may be conveniently divided into two classes :—

(1) Plants in which the gases are absorbed in towers, as in the Mitscherlich and Ritter-Kellner processes. In these the gas is first cooled by passing up and down a cooling pipe, and then up a tall saturating tower, 150 ft. high and 10 ft. or 12 ft. across and supported on wooden

scaffolding. These towers are filled with blocks of limestone (calcium carbonate) and dolomite (calcium and magnesium carbonates). The gas passes up the tower while water trickles down from above, and the liquor collects in a reservoir underneath. The strength of liquor produced in summer is 4 B. to 5 B.; in winter it is stronger, as high as 7 B., owing to the more complete absorption of the gas in cold water in which it is more soluble.

(2) Plants in which the gases are absorbed in tanks. Plants on these systems have been devised by Flodquist, Turner, Dougall, Frank, Partington, Stebbins and Barker. They are provided with artificial means for cooling the gases, and usually work with milk of lime in place of limestone. They produce, as a rule, stronger liquors of more constant composition than the towers; thus Frank's plant produces a liquor of 10 B. and stronger. The gas is led alternately into one of two tanks passing first into that containing the stronger liquor. When saturated this is removed and refilled with fresh lime liquor and the order of the passage through the tanks reversed. The gas may also be absorbed in towers, the milk of lime entering at the top and the gas at the bottom.

Strength of Liquors.—This will depend upon the method of boiling. In the Mitscherlich process a liquor of the following composition is frequently used :—

	Per Cent.
Total sulphurous acid	3·20
Combined ,,	1·14
Available ,,	2·06

For other processes stronger liquors are required. The efficiency of the liquor, as already stated, depends upon the percentage of available acid. Thus a liquor of the following composition, with a specific gravity barely 5 B. :—

	Per Cent.
Total sulphurous acid	3·25
Combined ,,	·87
Available ,,	2·38
Lime in combination	·76

was found to be as effective as a liquor of 7 B. with the following composition :—

	Per Cent.
Total sulphurous acid	4·35
Combined ,,	2·00
Available ,,	2·35
Lime in combination	1·75

Analysis of Sulphite Liquors.—The determination of the specific gravity is only a rough method of determining the strength of sulphite liquors, as it is merely a means of measuring the total amount of dissolved substances without distinguishing between them; thus it does not show in what proportions sulphurous acid is free and combined. An accurate and complete analysis of sulphite liquor is rapidly made by a titration method. In the first place, 10 c.c. of liquor are diluted to 100 c.c. with recently boiled distilled water, and 10 c.c. of this (=1 c.c. original liquor) is further diluted with distilled water and titrated with a decinormal solution of iodine, prepared by dissolving 12·7 grams in water with the aid of 18 grams of pure potassium iodide and making up to 1 liter. The $\frac{N}{10}$ iodine is run into the sulphite liquor from a burette until the faintest permanent yellow tinge is produced. The end reaction is more easily determined, especially by night light, if a little starch solution be added. The slightest excess of iodine then produces a permanent blue colour. The number of c.c. of iodine solution required are noted, and when multiplied by ·32 give the percentage total sulphurous acid in the liquor.

The blue colour of the solution is now destroyed by the addition of a trace of sulphurous acid and the acid present estimated by titrating with decinormal caustic soda, with methyl orange as an indicator. The solution before titration will contain a quantity of $\frac{N}{10}$ hydriodic acid equal to that of the $\frac{N}{10}$ iodine added, and also a quantity of sulphuric acid equivalent to the available sulphurous acid in the original liquor. To determine, therefore, the amount of sulphurous acid, subtract from the total amount of decinormal soda added the number of c.c. of decinormal iodine used in the previous titration; this will give the amount of decinormal soda required to neutralise the free sulphurous acid (in the form of sulphuric acid). As before, multiply each c.c. decinormal soda required by ·32, which will give the percentage of free sulphurous acid (SO_2) in the liquor. *Example.*—1 c.c. of sulphite liquor required 10 c.c. decinormal iodine to produce a blue shade with starch; this corresponds to (10 × ·32) = 3·2 per cent. SO_2. On titrating the acid liquor with decinormal soda, 15 c.c. were required; therefore 15 − 10 = 5 c.c. soda were required to neutralise the sulphuric acid corresponding to available sulphurous acid equal to (5 × ·32) = 1·6 per cent. available SO_2. To determine the lime in combination it is only necessary to multiply the percentage of combined sulphurous acid by $\frac{28}{32}$. Thus $1{\cdot}6 \times \frac{28}{32} = 1{\cdot}4$, therefore the composition of the liquor under examination was—

	Per Cent.
Total sulphurous acid	3·2
Combined ,,	1·6
Available ,,	1·6
Lime in combination	1·4

The free sulphurous acid can also be titrated with caustic soda solution with phenol-phthalein as an indicator.

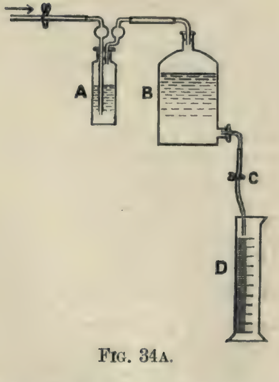


FIG. 34A.

Besides testing the sulphite liquors it is necessary to keep a check on the working of the sulphite liquor producing plant by examining the gases leaving the burner just before they enter the absorption vessels and after leaving the absorption vessels.

By comparing the figures obtained the percentage of gas escaping unabsorbed may be calculated, thus if 8 per cent. of SO_2 be found in the gases on entering and ·004 on leaving, this will mean a loss of $\frac{\cdot 004}{8} \times 100 = \cdot 05$ per cent.

For the purpose of testing, a portion of the gas before it reaches the absorption vessels is withdrawn through a small pipe inserted in the flue. Bandelin employs the following arrangement of apparatus, when the gases in the flue are under a small vacuum. The pipe from the flue leads to a glass-stoppered wash bottle, A (fig. 35) of about 300 c.c. capacity in connection with a tubulated flask of about 2 liters capacity, B. A is about half-filled with water with the addition of about 10 c.c. $\frac{N}{10}$ iodine solution and a little starch liquor. By running water out of B by opening the pinch cock C, a suction is produced and the gas from the flue is drawn through A until the blue colour just disappears when the pinch cock is closed again. This clears the air out of the apparatus as far as A. 100 c.c. $\frac{N}{10}$ iodine are now run into A and the stopper replaced. The pinch cock is then opened and the water from B allowed to flow into the empty graduated cylinder D until the liquid in A is again decolorised. The volume of liquid collected represents the volume of gas sucked through B which contains sufficient sulphurous acid to decolorise 100 c.c. $\frac{N}{10}$ iodine.

$$\frac{11{\cdot}14 \times 100}{\text{c.c. water} + 11} = \text{volume per cent. } SO_2 \text{ in the gas.}$$

This calculation applies for a temperature of 0° C. and for a temperature of 15° C. ½ per cent. more must be added to the result. For testing the gases when leaving the absorption apparatus only 10 c.c. $\frac{N}{10}$ iodine should be put into the wash bottle A as the gases are much weaker in sulphurous acid and the formula becomes $\frac{11{\cdot}14 \times 10}{\text{c.c. water} + 11}$ = volume per cent. SO_2.

Where the absorption plant is working under pressure instead of a slight vacuum, as described above, the gas to be tested is first blown through a series of three Winchester quart bottles connected together with rubber tubing. As soon as the air is wholly expelled, the connection with the flue is cut off and the sample of gas now under atmospheric pressure is drawn off from the last bottle and tested as described above.

Sulphite Boilers.—The conditions of sulphite boiling will depend upon whether the operation is carried out on the

Mitscherlich slow-cook system or on one of the quick-cook systems. The Mitscherlich boilers are usually horizontal. Those I have seen have a capacity of 90 cubic meters (19,800 gallons) and take 48 to 50 cubic meters of piled wood, but they are often made to take twice this quantity. The wood is first steamed (8 to 10 hours); it is then heated by indirect steam, taking 18 to 28 hours. The actual boiling, which proceeds at a pressure of about 45 lb. to 52 lb. per square inch at a temperature of 114° to 120° centigrade, takes 40 to 50 or 32 to 37 hours respectively, according to the pressure and temperature. At the lower pressure and temperature the boil takes altogether 75 to 85 hours, at the higher pressure and temperature 55 to 60 hours. At most not more than 7 or 8 boilings can be made per month. The accompanying table gives the details of a boil made on the Mitscherlich system:—

TABLE XLIV.

BOILING NO. 207 IN A HORIZONTAL DIGESTER (SCHUBERT).

		Pressure. Lb. per Sq. In.	Temperature. Degrees Centigrade.
23rd April,	11.30 A.M.	0	45
	8 P.M.	8·8	72
24th April,	1 A.M.	11·0	85
	6 A.M.	14·7	96
	11.30 A.M.	22·1	105
	2.30 P.M.	25·7	108
	6.30 P.M.	29·4	112
25th April,	1 A.M.	36·8	115
	6 A.M.	41·2	116·5
	9 A.M.	44·1	119
	12 NOON	41·2	120
	3 P.M.	33·1	119
	10 P.M.	30·9	118

Filled 22nd April, from 1.30 to 11 P.M., 88 cubic meters wood in chips, 9 cubic meters wood in shavings.

Steamed from midnight to 8 A.M. 23rd April.

Acid of 5° B. run in from 8 to 11.30 A.M.

After 27 hours temperature reached 68°.

After 48·5 hours temperature reached 120°.

Time taken to reach maximum temperature 21½ hours.

After 58·5 hours boiling temperature stood at 118°.

Time taken to finish boil, 10 hours.

Total time of boiling, 31·5 hours.

Highest pressure, 44·1 lb. per square inch. Highest temperature, 120° C. Cellulose, very fair.

More recent Canadian practice employs a higher pressure, 55 to 60 lb., the cooking process taking 18 to 35 hours.

In the quick-cook processes smaller boilers are mostly used, and as the liquors are stronger they can be heated by direct steam without diluting them too much. An ordinary digester taking two cords of wood chips will require 2500 gallons of liquor 10° Tw. containing 3½ per cent. sulphurous acid. The maximum pressure will be 65 to 85 lb., the temperature 300° to 330° F. The boilers are either fixed vertical digesters or cylindrical rotary digesters of varying sizes but smaller than the Mitscherlich boilers. To ascertain the right moment to shut off steam from a boiler it is necessary to draw off a little of the liquor and test it from time to time for the percentage of sulphurous acid. This must not fall below a certain figure which, however, will depend on conditions such as the type of boiler, kind of lining, the variety of wood and the condition in which the pulp is required.

Bandelin gives the following figures for a small rotary lead-lined digester.[1]

TABLE XLV.

CONDITION OF PULP IN A SULPHITE BOILER IN RELATION TO THE AMOUNT OF SULPHUROUS ACID IN THE LIQUOR.

c.c. $\frac{N}{100}$ iodine.	Per Cent., SO_2.	Remarks.
20	·64	The pulp is not ready for emptying.
19·5	·62	
19	·61	
18·5	·59	
18	·58	
17·5	·56	
17	·54	
16·5	·53	
16	·51	
15·5	·50	
15	·48	
14·5	·46	
14	·45	
13·5	·43	
13	·42	
12·5	·40	
12	·38	The pulp *can* be emptied, but is still somewhat coarse.
11·5	·37	
11	·35	
10·5	·34	

---

[1] *The Paper Mill*, 18th May, 1907, p. 20.

TABLE XLV. (*continued*).

c.c. $\frac{N}{100}$ iodine.	Per Cent., SO_2.	Remarks.
10	·32	The pulp is ready if not required for bleaching.
9·5	·30	
9	·29	
8·5	·27	
8	·26	The pulp is ready if required for bleaching.
7·5	·24	
7	·22	
6·5	·21	
6	·19	
5·5	·18	
5	·16	
4·5	·14	
4	·13	
3·5	·11	The pulp begins to become discoloured.
3	·10	
2·5	·08	
2	·06	
1·5	·05	
1	·03	The pulp is "burnt".
0·5	·02	

To test the liquor 5 c.c., which should always be taken from the same part of the digester, preferably the lower manhole, are diluted to 500 c.c. in a measuring flask and 100 c.c. of this (= 1 c.c. original liquor) titrated with $\frac{N}{100}$ iodine in the usual manner. The figure obtained multiplied by ·032 gives the percentage SO_2 in the liquid.

Properties of Sulphite Pulp.—The yield of sulphite pulp is higher than soda or sulphate, 1 cubic meter of piled wood yielding 135 to 170 kg. air-dry pulp (say 45 to 50 per cent. on the weight of the wood). The accompanying table gives an analysis of Mitscherlich- and quick-boiled pulps, also the percentage yield of sulphite pulp from different woods. A point worth noticing is the much larger proportion of resin found in sulphite as against soda and sulphate pulps, sulphite pulp containing ·45 to ·7 per cent., while the latter contained on an average ·05 per cent. or less. Bleaching the pulp reduces the quantity of resinous matter, but only very slightly.

TABLE XLVI.

PERCENTAGE YIELDS OF SULPHITE PULP FROM DIFFERENT WOODS (LABORATORY EXPERIMENTS—GRIFFIN AND LITTLE).

(The wood was boiled in a small experimental lead-lined digester of bronze with a capacity of about 12 liters.)

Spruce	50·75
Poplar	55·18
Cottonwood	50·80
Gum	45·73
Beech	42·80
Birch	53·80
Maple	52·61

PERCENTAGE YIELDS OF SULPHITE PULP AND QUALITY OF PULPS FROM DIFFERENT CONIFEROUS WOODS.

(Average figures from data published by Henry E. Surface.)

(The boiling was carried out in 65 gallon digesters, that is, on a relatively large scale.)

Species.	Yields Per Cent.	Quality of Pulps, Per Cent.			
	Screened Pulp.	Ash.	Cellulose.	Bleach Required.	Loss on Bleaching.
Bald cypress	45·2	7·9	76·4	89·0	8·3
Cotton gum	33·4	·97	82·8	26·9	3·8
Douglas fir	35·8	1·25	—	70·0	11·9
Engelmann spruce	42·5	·98	86·7	15·5	3·2
Grand fir	42·9	1·62	72·8	43·6	6·9
Hemlock	41·5	·56	83·5	61·0	7·4
Incense cedar	31·7	1·70	76·9	—	—
Jack pine	43·5	—	—	—	—
Loblolly pine	—	1·68	81·7	56·5	8·9
Lodgepole pine	40·0	1·93	79·4	31·9	6·5
Red spruce	—	1·54	81·3	50·0	10·6
Scrub pine	—	·72	—	50·8	6·9
Tamarack	45·3	—	—	—	—
Western hemlock	41·3	1·34	83·8	43·6	7·6
White fir	43·9	·91	85·7	20·1	3·3

TABLE XLVI. *(continued)*.

PERCENTAGE YIELDS OF SULPHITE PULP AND QUALITY OF PULPS FROM DIFFERENT DECIDUOUS WOODS.

(Average figures from data published by Henry E. Surface.)

(The boiling was carried out in 65 gallon digesters, that is, on a relatively large scale.)

Species.	Yields Per Cent.	Quality of Pulps, Per Cent.		
	Screened Pulp.	Ash.	Bleach Required.	Loss on Bleaching.
Aspen	50·0	·85	8·1	1·1
Beech	45·1	·79	14·4	2·3
Cotton gum	—	1·62	24·8	1·6
Douglas fir	45·7	—	—	—
Engelmann spruce	40·4	·74	67·9	6·8
Grand fir	43·2	·59	50·2	6·0
Incense cedar	38·3	·84	85·0	9·1
Jack pine	50·0	—	—	—
Loblolly pine	45·4	—	—	—
Lodgepole pine	40·8	·79	46·4	5·2
Longleaf pine	48·6	—	—	—
Red alder	42·5	·74	21·1	2·8
Red maple	43·6	·77	13·6	—
Sycamore	44·4	1·17	14·7	3·2
Tamarack	36·4	8·7	—	—
Tulip tree	41·1	1·42	15·9	2·8
Western hemlock	44·1	—	66·4	—
White fir	49·0	—	—	—

ESPARTO.—Esparto is either tied up into loose bundles or packed in bales. In the former case 4 to 5 "tons of measure" go to every ton weight. Taking 1 ton of measure, equal to 40 cubic feet, it follows that the weight thus packed is 11·2 lb. per cubic foot. When packed into bales under hydraulic pressure and bound with iron hoops, 22½ lb. go to the cubic foot.

The percentages of cellulose obtained from esparto from different sources are, according to Cross and Bevan—

TABLE XLVII.

Percentage Yield of Cellulose from Esparto.

	Per Cent.
Spanish	58
Tripoli	46·3
Arzew	52
Oran	49·6

Esparto is picked over by hand, dusted and treated in vomiting boilers generally built to take two or three tons; other data will depend upon circumstances. The pressure usually employed varies from 20 to 45 lb. to the square inch; the time varies from 2 to 5 hours, and the proportion of soda about 10 to 12 per cent. of 90 per cent. causticity. The liquor usually contains 6 per cent. of caustic soda (NaOH) but it is sometimes found advisable to add a quantity equal to 5 per cent. in excess of this, in order that the waste liquors may flow better in the tubes of the evaporators attached to the recovery plant (see also *Soda Recovery*). On standing, the waste liquors separate a wax known as esparto wax which is a commercially valuable product and may be recovered. The yield of cellulose varies, but may be put at 40 to 45 per cent. According to Beveridge, on an average 100 parts of grass yield 43 to 50 parts of finished paper.

Straw.—The straws mostly used as raw materials consist of oat, wheat, rye, and barley. The composition of straw varies enormously, not only in the different varieties of straw, but in straws from the same plant grown on different soils. Analyses of various straws must be taken only as approximate. The accompanying analyses are frequently quoted :—

TABLE XLVIII.

Composition of Straw (Hoyer).

	Wheat.	Barley.	Rye.	Oats.	Maize.
Fibre	51·0	49·0	47·0	47·0	40·0
Encrusting matter	40·0	38·0	45·0	32·4	40·0
Water	6·0	9·0	5·5	16·0	16·3
Silica	3·0	4·0	2·5	4·6	3·7

TABLE XLIX.

COMPOSITION OF STRAW (MÜLLER).

	Winter Rye.	Winter Wheat.	Summer Barley.	Winter Barley.	Oats.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Water	14·3	14·3	14·3	14·3	14·3
Ash	3·2	5·5	—	5·5	5·0
Fat, etc.	1·3	1·5	1·4	1·4	2·0
Albumenoids	1·5	2·0	3·0	2·0	2·5
Carbohydrates	25·7	28·7	31·3	28·4	36·2
Cellulose	54·0	48·0	43·0	48·4	40·0
Per cent. of dry cellulose on dry straw	63·0	56·0	50·1	56·4	46·6
Per cent. of air-dry cellulose on air-dry straw	60·0	53·3	47·7	53·7	44·4

Air-dry cellulose containing 10 per cent. of moisture. Air-dry straw containing 14·3 per cent. of moisture.

The percentage of silica in straw is particularly noteworthy; the fibre is also slightly lignified, so that the treatment of straw for the production of straw cellulose requires to be drastic. This, however, does not apply to the inferior product used in the preparation of straw boards and inferior classes of paper.

Yellow Straw Pulp.—For the production of straw boards the straw is boiled with lime.

(1) This may be done by boiling in open vats, the straw being put in between layers of lime, and the whole heated by passing in steam. This primitive process is now largely replaced (2) by boiling in rotary boilers. The straw is cut up into short lengths (3 to 5 cm.) and heated under pressure of 60 to 70 lb. for 2 to 10 hours. The amount of lime required may be taken as 10 to 16 per cent. on the weight of the straw. The yield of fibre varies from 60 to 80 per cent.

Straw Cellulose.—In the production of straw cellulose the raw material goes through preliminary processes on the same lines as esparto, consisting of cleaning, cutting, and dusting. The straw is boiled in rotary, cylindrical or spherical boilers taking anything from 1 to 5 tons of straw. The straw is sometimes first treated with hot water before the actual boiling. The treatment varies considerably with the variety of straw. The boiling may be carried out either by the soda, sulphate, or sulphite process.

(1) *Soda Process.*—For this purpose the straw is boiled under a pressure of 60 to 120 lb. for 6 to 8 hours; for 100 parts of straw 13 to 16 parts of caustic alkali are required; the liquor stands at 6 to 14 B. With stronger liquors the yield of cellulose is lower but the quality rather better. The ordinary soda-recovery process is applied to the spent liquors (see *Soda Recovery*).

(2) *Sulphate Process* (Dahl).—The straw is boiled with a liquor of 5 to 8 B. for 3 to 8 hours under a pressure of 30 to 80 lb. (see also sulphate process under WOOD PULP).

(3) *Sulphite Process.*—The liquor used has a density of 2·5 B., and the straw is boiled from 4 to 6 hours.

The yields of straw cellulose vary. The following may be taken as average figures (soda process):—

TABLE L.

YIELDS OF STRAW CELLULOSE.

	Per Cent.
Oats	43
Wheat	45
Rye	46
Barley	40

TABLE LI.

ASH IN COMMERCIAL PULPS (W. HERZBERG).

	Per Cent.
Sulphite (1)	0·48
„ (2)	0·51
„ bleached	0·42
Soda	1·34
„ bleached	1·40
Straw	2·30
„ bleached	1·34
Mechanical (pine)	0·43
„ (fir)	0·70
„ (aspen)	0·44
„ (lime)	0·40
Linen	0·76
„ bleached	0·94
Cotton	0·41
„ bleached	0·76

IRON IN PULPS (BEADLE).

Mechanical wood (aspen)	0·010
Bleached sulphite	0·008
„ „ (aspen)	0·012

The yield by the sulphate process is about 10 per cent. greater than by the soda process. When boiled with sulphite liquors by Schacht's process the yield is 15 to 20 per cent. greater. Straw was very little used in Great Britain, but the recent shortage of esparto has led to its reintroduction in some mills.

Flax Straw.—This material consists of the stems of the flax (*Linium usitatissimum*) grown for the production of the oil seed and commonly known as seed flax. The stems or straw are not suitable for retting and are usually burnt and destroyed on a large scale in the United States. Experiments have recently been undertaken for the utilisation of this material in the paper industry, particularly for the manufacture of stiff boards (fibre board or counter board).[1] It was found more economical to treat the straw mechanically to remove shive and convert it into flax tow as a preliminary to boiling. Boiling with about 15 per cent. of caustic lime was adopted at pressures up to about 100 lb., and the following table gives the conditions and yields both for straw and tow :—

TABLE LII.

YIELD OF WASHED FIBRE FROM FLAX STRAW, MEDIUM TOW, AND IMPORTED FLAX WASTE.

Material Tested.	Lime Used. Per Cent.	Time of Treatment. Hours.	Pressure per Sq. In. Pounds.	Yield of Washed Fibre. Per Cent.
Flax straw . .	18	6	100	41·2
Medium flax tow .	17	5	100	50·4
Imported flax waste .	10	10	45	55·7

The experiments were carried out on a large experimental scale and the counter boards made up on a commercial machine. They were of satisfactory quality and sold to the trade at the ordinary prices. The United

---

[1] *Utilisation of American Flax Straw in the Paper and Fibre-board Industry*, J. L. Merrill, U.S. Dept. of Agric. Bull. No. 322.

States flax crop is estimated to yield about 1,400,000 tons of the straw yearly.

Hedychium coronarium.[1]—This plant belongs to the Ginger family and grows in many tropical or subtropical districts, particularly southern Brazil, where it rapidly occupies districts which have been cleared, cultivated, and subsequently abandoned. It grows to a height of 6 ft. or more. The dried stem gives the following figures on analysis :—

TABLE LIII.

ANALYSIS OF HEDYCHIUM CORONARIUM.

	Whole Stem as Gathered. Per Cent.	After Passing Through Crushing Rollers. Per Cent.
Moisture	9·7	11·2
Ash	4·5	4·8
Cellulose	43·0	48·0
Extracted by chemical treatment .	42·8	36·0

corresponding to a yield of about 41 and 44 per cent. of air-dry cellulose on the air-dry material.

The fibres average about 2·6 mm. in length and in addition there are oval cells which can be stained blue like chemical wood, and shorter stouter fibres which stain yellow. The fibre is remarkable on account of its self-sizing properties. These are due to the small cells as, if completely removed by washing, the resultant waterleaf is not self-sized as in the case of material so treated as to retain these cells. The fibre yields papers of considerable strength compared with kraft papers, as will be seen from the accompanying table :—

---

[1] Beadle and Stevens, *Journ. R.S.A.*, Vol. LXI., Feb. 14, 1913; *Eighth Internat. Cong. App. Chem.*, Vol. XIII., p. 39; *Paper Maker*, Feb., 1914, p. 221.

TABLE LIX.

STRENGTH OF HEDYCHIUM CORONARIUM PAPERS.

Thickness.	Substance in Grams per Sq. Mm.	Substance in Lb. Demy. Lb.	Oz.	Bursting Strain in Lb. per Sq. In.	Elongation at Break. Per Cent.
·040	29·3	8	12	19·5	14·2
·065	52·0	14	6	46·2	15·1
·100	83·2	21	14	74·7	16·7
·146	118·2	31	14	102·3	18·4
·176	136·4	36	4	118·6	14·5

Cotton Hull Fibre (*Cotton Seed Cotton*).[1]—This consists of the half-grown or miniature seed hairs which remain attached to the shell or hull of the cotton seed after the greater part of the fibre has been removed by the ginning process. Attempts to recover these short fibres by chemical processes were quite unsuccessful but they are now separated mechanically by means of machines designed specially for the purpose. The loss on boiling is small and the fibre yields a paper similar to rag papers of good quality.

Dust-free Brazilian separated cotton yields 80-82 per cent. of bleached fibre, *i.e.* the same as lint cotton, with which it agrees in composition. On a large scale 75 per cent. yield of paper is obtained. The following table gives the length of cotton fibres obtained from the cotton-seed hulls of Brazilian seed when prepared for different purposes. The results are the mean of 40 measurements in each case.

		mm.
1.	Separated to produce "free" working	3·34
2.	„ „ „ "wet" „	2·62
3.	„ „ „ „ „	2·70
4.	The foregoing after conversion to half-stuff	1·93
5.	„ „ „ „ into writing paper	0·83
6.	Separated to produce "wet" stuff (another consignment)	2·27
7.	The above beaten to bruise fibres only, *i.e.* for strong stuff	2·20
8.	The above beaten to somewhat reduce length of fibres, *i.e.* for fairly thick writing paper	1·65

---

[1] Beadle and Stevens, *Journ. Soc. Chem. Ind.*, 1909, Vol. XXVIII., p. 1015.

Bamboo.—This material may possess great importance in the future as a raw material for paper-making on account of its abundance and the relative ease with which it is resolved for paper-making purposes. The chief difficulty met with lies in the nodes or knots which contain silicious matter. For this reason it is proposed to cut these out and to treat only the smooth lengths. The following figures give the cost of treatment for the production of unbleached pulp.

TABLE LV.

COST OF PRODUCTION OF BAMBOO PULP IN INDIA (RAITT).

	Rs.	A.
Bamboo	27	8
Chemicals	29	14
Fuel	17	4
Labour and superintendence	7	0
Depreciation and repairs	6	5
Royalty	1	0
Insurance, taxes, stores, and sundries	3	9
	92	8

or say £6 3s. 4d. per ton of 2240 lb.

The table on next page gives some idea of the sources of potential raw materials for paper-making.

SODA RECOVERY.

Soda recovery is applied to the waste liquors from boiling esparto, wood, and straw with alkalies. Rag liquors are also suitable for treatment, but the quantity of liquor obtained in an ordinary mill where rags only are used is insufficient for working a recovery plant on an economical basis. The liquors are obtained from draining and washing the pulp, and should, of course, be kept as concentrated as possible. Most of the fuel used goes to concentrate the liquors to such a point that they will take fire and burn continuously of themselves, the heat produced by the combustion of the organic matter being sufficient to drive off any remaining moisture and burn the residue to an ash. The desire to economise and recover the largest possible percentage of soda has led to the treatment of a larger proportion of wash waters from the pulp and the consequent production of weaker liquors for recovery. In the early days the strength of the liquors often reached 10° Tw. at 100° F., but nowadays 5° Tw. may be taken as more representative. The liquors require to be concentrated to at least 50° Tw. at 100° F. in order to maintain continuous combustion in the furnace.

TABLE LVI.

AVAILABLE SUPPLIES AND YIELDS OF CROP PLANTS (BEADLE AND STEVENS).

	Acres Under Cultivation.	Tons per Acre per Annum of Dry Raw Material.	Tons of Raw Fibre per Annum on Total Area.	Percentage Yield of Pulp on Dry Raw Material.	Tons of Pulp per Acre per Annum.	Tons of Pulp per Annum on Total Area.
Cropped once a year.						
Corn-stalks	30,000,000	1·0	30,000,000	12-18	0·12	3,600,000
Broom corn	178,584	3·0	450,000	32-40	1·00	150,000
Rice-straw	720,000	2·0	1,500,000	35	0·70	500,000
Flax-straw	2,000,000	1·0	2,000,000	30	0·30	600,000
Cotton hull fibres	—	—	150,000	75	—	112,000
Cotton-stalks	10,000,000	0·45	4,500,000	35-40	0·15	1,500,000
Hemp-straw	—	5·0	—	20	1·00	—
Hedychium	—	6-10	—	60	4·00	—
Cropped every 5 years.						
Bamboo (Pearson, Sindall)	—	$\frac{15}{5}$	—	45	1·35 to 1·57	—
Bamboo (Pearson, Raitt)	—	$\frac{8}{5}$ to $\frac{18}{5}$	—	45		—
Cropped every 40 years.						
Pulp wood	—	$\frac{16 \text{ cords}}{40}$	—	45	0·20	—

The ordinary liquors contain a large quantity of dark-coloured, complex, organic substances.

Davis gave the following figures for the average composition of liquors, the soda expressed as 46 per cent. soda ash, the liquor standing at 10° Tw. at 100° F. :—

TABLE LVII.

COMPOSITION OF LIQUORS FOR SODA RECOVERY.

	Esparto. Per Cent.	Wood. Per Cent.	Straw. Per Cent.
Soda ash (46 per cent.) . .	5	5·4	4·7
Organic matter . .	6	4·2	6·6
Water	89	90·5	88·7

Griffin and Little, in 1894, gave the following analysis of a partially concentrated wood liquor standing at 115° F. :—

TABLE LVIII.

COMPOSITION OF WOOD LIQUOR FOR SODA RECOVERY.

	Per Cent.
Water	83·51
Organic matter	5·96
Caustic soda	8·60
Black ash waste	1·93
Total	100·00

The density of these liquors may be expressed in degrees Tw. at 100° F., as suggested by Davis, as the strong liquors are almost solid at ordinary temperatures. The accompanying table (Davis) gives the gravity for two liquors of different strengths standing at 4° and 10° Tw. respectively, at 60° F., at different temperatures expressed as degrees Centigrade or Fahrenheit :—

TABLE LIX.

GRAVITY OF WASTE LIQUORS AT DIFFERENT TEMPERATURES.

°C.	°F.	°Tw.	°Tw.
15·5	60	4	10
20	68	$3\frac{3}{4}$	$9\frac{3}{4}$
40	104	$3\frac{1}{4}$	$8\frac{1}{4}$
60	140	$1\frac{3}{4}$	$6\frac{3}{4}$
80	176	0	$4\frac{3}{4}$
100	212	Below 0	$2\frac{1}{2}$

From this table it will be seen that a rise of temperature of 1° F. for density between 6° and 10° Tw. ,lowers the density on an average of ·05° Tw. For the lower temperatures it is ·04° Tw., and for the higher ·06° Tw.

I also give a table by Davis showing the gravity as degrees Tw. at 100° F. and corresponding compositions of liquors :—

TABLE LX.

GRAVITY AND COMPOSITION OF WASTE LIQUORS.

Tw. at 100° F.	Per Cent. of 46 per Cent. Ash.	46 per Cent. Ash.	Lb. per 1000 Gals. Organic Matter.	Water.
10	5·0	525	630	9·345
9	4·5	470	564	9·416
8	4·0	416	500	9·484
7	3·5	362	434	9·554
6	3·0	309	370	9·624
5	2·5	256	307	9·687
4	2·0	204	245	9·751
3	1·5	152	182	9·816
2	1·0	100	120	9·880

Soda-recovery plants are of two types. Of the first, the Porion evaporator may be taken as typical. The second, and more modern form, consists of a multiple-effect evaporator for concentrating liquors and a furnace for burning them to ash. In the Porion evaporator the hot gases from the furnace pass over a large tank containing the weak liquors; the tank stands in an evaporating chamber, and the space above the liquor is full of fine spray produced by small fans rotating rapidly near the surface. In this chamber the liquors are concentrated to 50° Tw. at 100° F. ; they then pass to the combustion chamber, which lies between the furnace and the evaporating chamber, where they are burnt to ash. In this plant 12 lb. of water are evaporated per lb. of fuel, and 7 lb. of water by the combustion of the dry organic matter in esparto liquor, so that actually some 22 lb. of water are evaporated per lb of fuel.

Multiple-effect plants are built on many different systems, the principle, of course, being the same in all cases. A quadruple-effect evaporating plant constructed by Ernest Scott & Co. works with a pressure of 30 lb. on the first effect ; the liquor is concentrated from 5° Tw. to

60° Tw. in one operation, the liquor being partially concentrated in each effect, and removed from the fourth effect by special pumps. With this plant 10,000 gallons of liquor can be dealt with for about 22 cwt. of coal.

In some cases the liquor from the multiple effect plant passes to a "disc" evaporator where the latter part of the concentration is effected before going to the roaster. The disc evaporator comprises plates connected to a revolving shaft which dip in and out of the liquor.

The modern form of roaster consists of a revolving furnace; the liquor from the multiple-effect plant passes continuously in and is discharged completely burnt to ash. The heat is mainly supplied by the burning liquor, the fuel consumption being 3 cwt. per ton of ash.

Causticising the Liquor.—The ash is extracted with water and the diluted liquor run into large iron vessels, where it is treated with lime and heated by live steam. The vessel may also be provided with stirrers. It is essential to have the liquor dilute if the causticising is to be complete; the strength of the liquor should not exceed 15° Tw. at 60° F. This will mean about 7·3 per cent. of soda ash, or 73 lb. of soda ash per 100 gallons; the lime used should be of good fat quality. Poor qualities are not only less effective, but produce a large proportion of sludge, in the removal of which part of the liquor is lost. The reaction between the lime and the soda ash consists in the formation of caustic soda and calcium carbonate. Sufficient time must be given for the reaction to complete itself, and the liquid must be kept well agitated and at boiling temperature. The liquor may be tested from time to time by withdrawing a portion, allowing the precipitate to settle and testing to see whether the liquor effervesces with acid. It is as well to continue heating for an hour after the liquid no longer effervesces; the quantity of lime required will depend upon the quantity of quicklime it contains, and the quantity taken should be rather in excess of that required theoretically. 80 per cent. to 90 per cent. of the causic soda used in boiling is recovered.

AMMONIA PROCESS FOR THE PRODUCTION OF CELLULOSE.

Patents were taken out by J. Koenig in 1912[1] for the treatment of wood by heating under pressure, first with a

---

[1] German Pat., 265, 483, Feb. 15, 1912.

solution of ammonia and then with a dilute mineral acid. It was claimed that this process can be successfully applied to the very resinous woods (e.g. *Pinus sylvestris*) and that the spent liquors on evaporation yield a valuable cattle food. At first sight, a process in which ammonia is used to replace soda or sodium salts would appear hopeless on account of the relatively high price of ammonia and the difficulty of recovery owing to its volatile nature. The inventor, however, apparently anticipates a considerable reduction in the price of ammonia following on the now commercially successful production of nitrogen products from the air.

Koenig and others have also patented processes for the production of cattle foods from sulphite liquors. That these waste products of the pulp mill possess an enormous potential value as food stuffs is unquestionable. It is merely a question of treatment for the removal of certain ingredients to make them digestible and palatable to cattle.[1] There is little doubt that these matters have been the subject of intensive research in Germany since the outbreak of the war and it is possible that we shall find that the problem has now been solved. It is obvious that the utilisation of the waste liquors would have a marked effect on the future production of wood pulp.

EXAMINATION OF CELLULOSE AND HALF-STUFFS.

During recent years methods have been worked out for the chemical examination of cellulose and half-stuffs. The chemical standards to be described are of considerable importance when the half-stuff is intended for the manufacture of cellulose products such as the various types of soluble cellulose, *viz.* viscose, cuprammonium cellulose, and proxylin as used in the manufacture of artificial silk, cellite sheets (transparent sheets of cellulose), etc. Also in the manufacture of nitrated celluloses for explosives.

Closely connected with these chemical tests is the bleaching capacity, treated of in the next section under

---

[1] It is found that the dried sulphite residues contain a bitter principle which makes them unpalatable, a purgative substance, and finally certain tannin substances which render them indigestible. It is said that the two former ingredients can be removed but the latter has not yet been successfully eliminated.

"Bleaching." Thus, a half-stuff giving a high copper value will not be easy to bleach economically.

Mercerisation Test (Alkaline hydrolysis) (Cross and Bevan).—This test was devised for the approximate separation of α and β cellulose, the α cellulose representing the more resistant constituent. The authors' instructions for carrying out the operation are as follows :—

Five grams air-dry material are macerated at the ordinary temperature with 50 c.c. of caustic soda solution containing 17·5 per cent. NaOH (= 40° Tw.) for exactly half an hour. The mixture is diluted with 50 c.c. of water and poured on to a cotton cloth supported on a perforated plate in a funnel connected with a filter pump. The fibrous mass is drained and successive quantities of water are poured on until the total filtrate amounts to about one liter. The fibre is washed with dilute acetic acid, and finally with water, and dried; it represents the α cellulose. The filtrate is acidified with acetic acid, and digested in the water-bath until the precipitate coagulates sufficiently to be collected on a cotton cloth filter. It is washed on the filter and detached for drying. This precipitate represents the β cellulose. The difference of the sum of α and β cellulose from the original is called γ cellulose. It may be regarded as a complex of modified derivatives of the original material.[1]

The authors point out that the separation is empirical as the optima conditions for the physical condition which allows of free filtration and circulation of the reagent are seldom met with.

Copper Value (Schwalbe).—The basis of this test is the power of hydro- and oxycellulose to reduce Fehling solution, the copper value being the amount reduced by 100 grams of cellulose. The test is carried through as follows :—

Two to three grams of the air-dry substance are placed in a round-bottomed flask with 250 c.c. distilled water. The flask is fitted with a stirrer and condenser. The condenser should be some form of internal condenser, as rubber and cork joints are not permissible, as they may give rise to reducing substances. While the contents of the flask are being heated to boiling, 50 c.c. of copper sulphate solution and 50 c.c. of alkaline Rochelle salt

---

[1] Cross, Bevan, and Briggs, *Papermaking*, 4th edition, pp. 97-8.

solution are heated in separate flasks. The boiling liquids are mixed and added to the cellulose mixture in the flask just as the latter begins to boil. The contents are kept stirred by some form of mechanical stirrer. The flasks are washed out with 50 c.c. of boiling water which is poured into the flask containing the cellulose. The cellulose and Fehling solution are now allowed to boil for exactly 15 minutes with the condenser in the neck of the flask. The latter is then removed and one gram of diatomite, shaken up with 50 c.c. of water, is added. The object of this is to prevent the cuprous oxide from passing through the filter paper. The contents of the flask are then filtered through a double filter paper with the help of a suction pump and washed with hot water until the filtrate no longer contains copper as shown by testing with a solution of potassium ferrocyanide. The residue of cellulose on the filter paper remains blue on account of copper salts which cannot be washed out. An allowance can be made for this (see next paragraph). The copper is dissolved from the mass on the funnel with dilute nitric acid (6·5 per cent.), or preferably the mass from the funnel is transferred to a porcelain dish and digested with the nitric acid on the water-bath till the cuprous oxide is dissolved. The mass is then replaced on the funnel and filtered, collecting the filtrate and washings and filtering the solution. It is found that nitric acid does not always remove the whole of the copper in this manner and it is advisable to digest the residue with ammonia and then treat with excess of nitric acid. The copper-containing filtrates are united and the copper contents estimated by one of the ordinary processes, after taking to dryness and gently igniting to destroy the organic matter dissolved from the fibre.

Copperhydrate or Cellulose Value.—This value gives the amount of copper retained by the cellulose when treated with Fehling solution in the cold. It corresponds to the copper salt retained by the cellulose and not washed out with water in the determination of the copper value. It may be determined separately by digesting 2 or 3 grams cellulose half-stuff with 100 c.c. of Fehling solution and 250 c.c. of cold distilled water for three-quarters of an hour with stirring, then adding the diatomite and proceeding as above in the determination of the copper value. All operations, however, must be carried through with cold and not hot water.

Note.—Purification of the diatomite (kieselguhr). The diatomite required in the above two estimations should be purified by first igniting and then digesting with Fehling solution. It is then thoroughly washed and finally treated with concentrated nitric acid and washed again. The diatomite is conveniently kept in a flask of water which is shaken up before adding to the cellulose.

Hydrolysis Value (Acid Hydrolysis) (Schwalbe).—Two to three grams of the air-dry substance are boiled for exactly one-quarter of an hour in a round-bottomed flask with 250 c.c. of a 5 per cent. solution of sulphuric acid. The filtrate is neutralised with caustic soda solution (10 grams in 25 c.c.), and 100 c.c. of Fehling solution added. The further procedure is the same as for the copper value.

A research to co-ordinate and compare the figures obtained in the above tests, with measurements of bleaching capacity, is greatly needed.

BLEACHING.

The common bleaching agent in general use is bleaching powder (for details of analysis, see pp. 78-81). The chemical constitution of this substance is not thoroughly understood. Bleach liquor is believed to contain calcium hypochlorite, but is said not to be so effective as a solution of the latter. In addition to bleach liquor the following bleaching solutions may be mentioned :—

Calcium Hypochlorite.—A solution of this substance is obtained by passing chlorine into milk of lime. It possesses certain advantages over ordinary bleach liquor, but the cost of carriage to mills in most cases prohibits its use. On the other hand, it is a convenient bleaching agent for mills situated in the neighbourhood of alkali works, where the cost of carriage is small. Being in the liquid form, it is more convenient to handle when once in the mill. According to Beadle, it is more effective than a solution of ordinary bleach containing the same amount of available chlorine.

Sodium Hypochlorite.—A solution of this substance may be prepared by adding a solution of sodium carbonate to ordinary bleach liquor. The lime is precipitated as calcium carbonate and allowed to settle out. According to theory, 53 parts of anhydrous sodium carbonate, or 143 parts of crystal carbonate, are required for a batch of liquor prepared from 100 parts of 35 per cent. bleaching powder. Sodium hypochlorite, like calcium hypochlorite liquor, is more effective than ordinary bleach. Beadle found that by converting bleaching powder into sodium hypochlorite the liquor prepared from 60 lb. of bleaching powder was as effective as ordinary bleaching liquor from 100 lb. of bleaching powder. He also made sodium hypochlorite for many months in a mill by precipitating bleach liquor with a solution of salt cake (sodium sulphate). The lime is precipitated as calcium sulphate in the form of pearl hardening, while the sodium hypochlorite remains in solution.

Electrolytic Bleach.—The liquors are prepared by electrolysis of salt solutions. Such liquors are said to be more effective than ordinary bleach liquor containing the same amount of available chlorine.

Electrolytic bleach may be more economical than the use of bleaching powder if the electric current can be cheaply produced and common salt is also to be had cheaply. There is a considerable waste of salt, as it is not economical to electrolyse more than part of the salt in solution. A low voltage, usually 100, is required for the cells but a number of cells can, of course, be placed in series and so a higher voltage current utilised.

An alternative method is to electrolyse the salt and keep the caustic soda and chlorine separate; the former is used for boiling the fibre and the latter is absorbed in lime or soda for the production of bleaching powder or sodium hypochlorite.

Keeping Properties of Bleach.—Bleach should be stored in a cool, dry place. Pattinson found a total loss of about 3 per cent. of available chlorine in twelve months with bleaching powder stored in sound casks and exposed to a range of temperature varying from 38° to 62° F. With respect to bleach liquor, this should be stored in covered tanks out of contact with the light. According to Beadle, such solutions may be kept for six weeks, except in hot weather, the loss of chlorine being almost inappreciable. After this time a rapid deterioration sets in. According to Lunge and Landolt, bleach liquor kept in the dark in a closed vessel remained practically unchanged for twenty-four days, and after thirty-three days had only lost less than a ½ per cent. In diffused daylight, even in closed vessels, decomposition sets in at once, and after thirty-three days only 8·5 per cent. remained of the 33 per cent. originally present. Much difficulty is experienced in keeping bleach in hot climates where deterioration is very rapid. It has been found that the addition of free lime to the bleach very much improves its keeping qualities.

Bleaching Fibres.—In order to expedite the bleaching process a larger proportion of liquor is taken than would be necessary if sufficient time were given for the bleach to exhaust itself. When bleaching rags, soda pulp, etc., the liquid may be heated to a temperature not exceeding 90° to 100° F. If the temperature is allowed to exceed this the cellulose is attacked, therefore when heating by direct steam every precaution must be taken to ensure thorough circulation and prevent local over-heating.

Although bleached liquors when hot act more rapidly than when cold, a larger proportion of bleach is consumed for the same amount of fibre bleached. On the other hand, a larger excess of bleach must be taken in the cold for bleaching at the same rate as when the pulp is warmed.

There is a paper mill maxim, "more water more bleach," and this is borne out by experimental tests, bleaching liquor being found to be more effective in concentrated solutions.

The bleaching action of ordinary bleach may be accelerated by the use of carbon dioxide. Good results are said to be obtained by discharging the gas under the roll of the hollander or potcher.

The chemical residues left in spent bleach liquor absorb chlorine from fresh bleach, although the spent liquor still contains some available chlorine; it is therefore a doubtful advantage to use spent liquors for making up fresh bleach, unless they contain a comparatively large proportion of available chlorine. They can, however, be added to the half-stuff in the breaker towards completion of the washing, and so utilised and washed out so that the residues do not affect the main bleaching which follows.

Chlorine Gas.—Bleaching may also be effected by means of chlorine gas, which is sold compressed in steel cylinders at 5 atmospheres at 15° C. The half-stuff from the machine is made into wet rolls, which are packed into a cement-lined chamber and then treated with the gas amounting to 2 per cent. of the dry weight of the fibre.

The manhole is closed gas-tight, as at first considerable pressure develops. After a few hours the gas is completely absorbed and a very good coloured half-stuff is obtained by the use of a little ordinary bleach in the beater. Thus for rag half-stuff, 2 per cent. of chlorine gas and 2 per cent. of bleach will replace the 12 per cent. of bleach ordinarily used.

Bleaching Capacity.—It is often important to determine the bleaching capacity or "bleachability" of a half-stuff or other fibrous material for the purpose of determining the consumption of bleaching powder (or active chlorine) necessary to produce a certain degree or standard of whiteness. The consumption of bleach will to some extent depend on the conditions under which it is applied, and it is therefore necessary to lay down a standard method of procedure. Some of those proposed may be described:—

(1) This method of testing is recommended by **Arnot**, particularly for wood pulps (*Paper Trade Review*, 1909, p. 657) substantially as follows:—

From each of the sample bales opened to test for moisture, one strip of pulp is cut, marked with the brand of pulp and boil number. The strips are torn into short pieces and mixed and 20 grams are carefully weighed out, *without previous drying* (this is essential, as the whole operation must be conducted as nearly as possible under the conditions obtaining in the mill, and from the moisture test, the dry contents being known, for exact comparisons one can at any time deduce the figure for dry weights). The pulp is then further reduced by tearing and splitting as much as possible, and stirred into 250 c.c. of water in a beaker glass or porcelain basin. The water must be the same as that used for manufacturing in the mill, and of the same temperature as is reached in the bleacher. The quantity was arrived at by determining the consistency of the stuff in the bleachers in the mill, and, as concentration has a marked influence on bleaching, this point must be carefully attended to, and the correct quantity of water to use must be determined for each individual mill.

To this watery pulp is then added an excess of bleaching solution, which has previously been titrated and whose content of available chlorine is accurately known. The whole is well stirred and then allowed to stand, or occasionally stirred till the pulp has attained the colour of a standard sample, which may be kept handy sealed into a clear glass test tube or sample glass. So soon as the colour is satisfactory the pulp is once more stirred round and 5 or 10 c.c. of the fluid withdrawn by a pipette after pressing the pulp to one side. The fluid withdrawn is then titrated. From the result, the whole contents of liquid being known, it is easy to reckon out the whole quantity of available chlorine still present, and this deducted from the available chlorine at first added gives the quantity required to bleach 20 grams, and this quantity multiplied by 5 gives chlorine per cent.

(2) Baker and Jennison (*Soc. Chem. Ind. Journal*, 1914, p. 288) suggest four standards of colour. The actual test is carried out as follows:—

"Minimum quantity to be taken, 10 grams.

"10 grams—10 per cent. air dry pulp.

"160 c.c. of water containing bleaching powder (35 per cent. chlorine) equivalent to 12 per cent. of bleaching powder on the pulp taken.

"Temperature—100° F. Time of bleaching—2 hours."

The pulp should be torn into shreads by hand, "throwing into a liter of water, agitating with a powerful egg beater made of brass, and fitted with teeth, until a uniform pulp is obtained. Throw the resultant pulp into a porcelain filter and exhaust with the water pump, finally squeezing by hand, leaving the pulp approx. 30 per cent. dry. Place in a suitable vessel which is standing in a water bath, and is at the temperature of the bath, *i.e.* 100° F. Take 100 c.c. of water at 105° F., add the requisite number of c.c. of bleach solution to give the required percentage, and pour on to the pulp. Stir well, and bleach for two hours at 100° F., stirring occasionally with the thermometer.

"With filtered mill solution at 4½° Tw. approximately 30 c.c. of bleach solution will be required. This is checked at the time of the experiment.

"After the time has expired throw the bleached pulp upon the porcelain funnel, exhaust with the pump, wash, make the filtrate and washings to 2 liters and titrate an aliquot portion. Calculate the bleach consumed as percentage on the 10 per cent. air-dry pulp taken.

"Make suitable sheets of the pulp for reference, and it is important to note that these should be air-dried."

Proportion of Bleach Required.—It will be understood that the proportion of bleach required for any particular fibre will vary very much with the circumstances. The accompanying table gives the quantities of bleaching powder required for 100 lb. of different fibres. The quantity of bleach will, however, depend on the previous treatment, especially the boiling process :—

TABLE LXI.

QUANTITIES OF BLEACHING POWDER REQUIRED FOR 100 LB. RAW MATERIALS (GRIFFIN AND LITTLE, IN 1894).

	Lb.
Rags	2-5
Straw	7-10
Esparto	10-15
Soda poplar	12-15
,, spruce	18-25
Sulphite poplar	14-20
,, spruce	15-25
Jute	10-20

QUANTITIES OF BLEACHING POWDER REQUIRED FOR 100 LB. RAW MATERIALS (SINDALL, IN 1906).

	Lb.
Rags	4-5
Straw	8-14
Esparto	5-10
Soda pulp	15-25
Sulphite pulp	7-18

2 to 5 lb. probably represent the average usually required for rags, although larger quantities may be necessary when dealing with exceptionally dirty material. In some mills an addition of mineral acid is made. The quantities used in Germany are 4 parts concentrated sulphuric acid diluted with 16 parts of water to every 100 parts of bleaching powder.

Soda pulps are more difficult to bleach than sulphite pulps ; indeed, it is very difficult to get soda spruce of a good colour. Müller gave the following figures for the percentages of bleach required for wood pulps :—

TABLE LXII.

QUANTITIES OF BLEACHING POWDER REQUIRED FOR WOOD PULPS.

	Per Cent.
Soda pulp	14-18
Sulphate pulp	10-15
Sulphite ,,	14-22

It is the practice in some mills to bleach soda pulp twice where a good colour is required. In the first operation 16 per cent. of bleach is taken, and in the second operation 8 per cent. or even more.

Griffin and Little give 7 to 10 per cent. as the proportion of bleach used with straw, but the German authorities quote higher figures, 12 to 30 per cent. It is also recommended to bleach with two or three separate lots of liquor equal to 4 or 5 per cent. of powder on the weight of the material instead of adding the whole of the liquor at once. 2 to 12 per cent. of sulphuric acid may be used on the weight of the straw, and the liquors are generally taken stronger than for rags.

For esparto 6 to 12 of bleach is required.

Various attempts have been made to bleach mechanical pulp, but with little success. Many mills, however, impregnate the pulp with a small quantity of bisulphite liquor as the sheet leaves the cylinder of the board machine. For 100 kg. dry pulp 2·5 kg. concentrated sodium bisulphite liquor 38 B. is taken, diluted with 20 or 30 times its volume of water.

BEATING.

Every papermaker is familiar with the beaterman's hand tests for ascertaining the length of the fibre and degree of "wetness" or "freeness" of the pulp at various stages of beating.

During the last few years attempts have been made to construct an instrument which will give a measure of the condition of the beaten pulp. Thus a known volume, say 1000 c.c., of the pulp taken direct from the beater may be poured into a 1000 c.c. graduated glass cylinder with a false bottom made of ordinary machine wire. If the pulp is slimy and wet, it may be better to take an aliquot part of 1000 c.c. and dilute it to 1000 c.c., well mixing before using. The pulp will drain rapidly at first and then more slowly, and the volume of the pulp remaining when the dripping has ceased may be measured. If preferred, two measurements may be made, one when the liquid ceases to run and commences to drip, and a second when it has ceased to drip. Instead of measuring the volumes of pulp left in the cylinder, it is more convenient to collect the (1) running and (2) dripping water separately and measure the volumes afterwards.

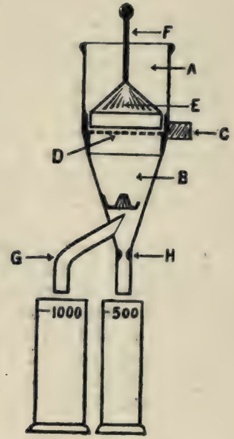


FIG. 36.—Beaten Stuff Tester.

A more complicated apparatus (Schopper-Riegler), constructed for the same purpose, is shown in the illustration. It consists of a cylindrical vessel A, fitting on to a funnel B which is suitably supported at C. The upper end of the funnel is fitted with wire gauze D. The pulp (when necessary first diluted with a definite proportion of water), is poured into A but cannot pass through because the gauze is blocked with the conical stopper E. When this is lifted by means of the handle F, the water runs through into the funnel, the pulp being caught on the gauze. At first, while the water is running fast, almost the whole of it escapes by the wide side tube G into the 1000 c.c. measuring cylinder; very little finds its way into the 500 c.c. cylinder through the constricted part H at the bottom of the funnel. Later, the water drains off from the pulp much more slowly and the level of the water collecting in the funnel sinks below that of the outlet tube G; from that moment onwards, all the water which drains away collects in the 500 c.c. cylinder. In this manner the fast running water is collected and measured in one cylinder and the slow running in the other.

Taking, in one instance, unbeaten ordinary sulphite pulp, the fast water collected in 10 seconds amounted to 870 c.c. The same pulp after beating for 8 hours gave only 120 c.c. of fast running water.

Klemm suggests defining the state of the beaten stuff as an arbitrary scale, taking a material which yields only fast running water at zero and one yielding no fast running water at 100. All conditions of freeness or wetness of pulp will lie between these figures, in accordance with the volume of fast running water, and the condition may be defined as the "degree of beating." It is found that with sulphite pulp the degree of beating is directly proportional to the time of beating up to 6 hours, after which the degree of beating increases less rapidly. The amount of pulp taken, that is to say the concentration of the fibre in the liter of pulp taken for the test, has some influence on the result; higher concentrations giving higher degrees of beating while higher temperatures have the reverse effect, as might be expected from a reduction in the viscosity. The influence of the temperature appears to be relatively small, a reduction of about 5° of beating corresponding to a rise of temperature from 10° C. to 30° C., which covers ordinary temperature variations in the mill. Only a few experimental data are at present available and it is not yet possible to estimate the value of this and similar appliances in mill practice. From the foregoing it appears that a simple apparatus can be easily constructed for preliminary experimental work. It is possible also that the time taken for a definite amount of pulp to drain may yield as valuable results as a measurement of the volumes of fast and slow running water in the manner described.

COLOURING PULP.

The colours used are either mineral, vegetable or synthetic dyes prepared from coal-tar.

Mineral colours load the paper at the same time as they colour the pulp. As a class they are the most permanent to light. The more important have been described. In many cases, however, it is preferable to form the mineral colour in the pulp by a chemical reaction between the ingredients which are dissolved and added separately. Examples of this are: Yellow and orange chrome, produced by adding first a solution of sugar of lead or lead nitrate to the pulp, followed by one of potassium or sodium bichromate. Suitable proportions are 20 parts sugar of lead to 6 parts bichromate. The further addition of milk of lime or caustic soda produces an orange shade.

Iron oxides or hydroxides of various shades of buff or brown are produced by the interaction of iron salts and lime or soda. With copperas the brown colour is only slowly developed as the ferrous hydroxide gradually oxidises in the beater.

Manganese browns are similarly produced from "still liquor" or manganese chloride and alkalies.

Prussian blue is obtained by first precipitating iron oxide in the pulp by means of copperas, then adding a solution of yellow prussiate of potash, and finally souring the pulp with sulphuric acid. The following proportions are given by Erfurt: 3 parts copperas, 2 parts prussiate, and 1 part sulphuric acid 168° Tw. Vegetable colouring matters are now very little used, but the tannins are of some importance. In the case of catechu (cutch) and quercitron a yellow colouring matter is combined with tannin. They are used for dying brown and dark shades with various mordants, such as bichromate and nitrate of iron. In this connection advantage is taken of the dark-coloured compounds formed by tannins and iron salts to produce colours more or less approaching black. Logwood extract gives dark shades with different mordants, but they are not so fast to light as those first mentioned.

Coal-tar Colours for Paper Pulp.—Some account of the nature of coal-tar colours has been given. There remains to be considered the dyes best suited for colouring paper pulp and their economical application.

One of the first considerations is a colourless backwater which results when the dye is properly fixed on the fibre. Cellulose itself has very little affinity for coal-tar dyes, and there are only a few, such as the substantive Azo dyes derived from benzidene, etc., which can be used for unsized papers. On the other hand, the resin or aluminium resinate deposited on the fibres in the ordinary process of engine-sizing has a much greater affinity for coal-tar dyes and acts as a mordant in fixing the colour. The effect, however, will depend on the order in which the ingredients, size, alum, dye and loading, are added. Other substances, such as common salt, Glauber's salt (sodium sulphate) and copper sulphate, are sometimes added to the beater to aid in fixing the colour. Tannins are also used as mordants, especially for saddening the bright hues of coal-tar colours. Further, as some dyes are rather sensitive to acids, too large an excess of alum must be avoided, while in other cases a large excess of alum is necessary to bring out the full effect of the dye. Fillers also play an important part. They have a considerable affinity for the basic dyes, combining with them to form lake colours, and help to distribute the colour evenly throughout the pulp.

As a general rule, the dye is best added to the pulp before the size. Loading materials are added after the dyeing, but before the sizing. If added in the reverse order, two or three times as much dye may be required with heavily loaded papers, but no general rule can be given which is applicable to all cases.

Basic colouring matters are used both for sized and unsized papers; their colouring power is high, and they are suitable for cheaper classes of paper. They are not so fast to light as acid colours, but are more easily fixed. They are susceptible to acids, and alum must be used sparingly.

Acid colouring matters are not so readily fixed on the fibre as the basic ones. Their use is restricted to hard-sized papers. They are, relatively speaking, fast to light.

The eosine colours are mostly used for shades of pink and red, and here again alum must be used sparingly. Addition of borax is recommended for reducing the effect of the alum and increasing the intensity of the colours.

Substantive colours are those which dye the fibre direct without the use of a mordant; they consequently find application for unsized papers. Although they possess an affinity for the fibre and are readily fixed on rag or chemical pulp, they are imperfectly fixed on mechanical pulp.

On the other hand, the basic dyes have a greater affinity for mechanical pulp and unbleached cellulose. They dye it a deeper shade than the purer forms of cellulose, especially with soft-sized papers. The difference between mechanical wood, unbleached chemical wood, jute, etc., on the one hand, and bleached cellulose, rag, etc., on the other hand, is, shortly, this: The former have a natural affinity for certain dyes on account of the encrusting matter they contain, and are therefore more strongly dyed in unsized or soft-sized papers than the latter. Encrusting matters hinder the mordanting of the fibre, and therefore when mordanting with rosin size the encrusting fibres do not take the colour so well as bleached cellulose, especially in hard-sized papers.

Coal-tar dyes are generally dissolved in hot water. In most cases the water may be heated to boiling without injuring the dye. Hard water is detrimental to many colours, and condensed water from the engine may be used for dissolving the colour, if no better form of soft water is at hand. Acid colours are less affected by the dissolved lime salts than basic colours, and if only hard water is available basic colours should be made into a paste with dilute acetic acid before pouring boiling water on to them. The dye is placed in a wooden tub or earthenware vessel; about ten gallons of water are taken for every pound of dye, as a general rule, although it is possible to do with less. The mixture is thoroughly stirred until the dye is completely dissolved. The quantity of dye required will vary with the make and the shade it is required to produce; ½ to 2 per cent. on the weight of the paper usually produces average shades, and quantities exceeding 5 per cent. are seldom required, except for very intensely coloured papers. Where a mixture of two or more dyes are required they are almost always dissolved in different receptacles and added separately to the beater, as many dyes react, chemically precipitating one another, when their solutions are mixed. This mutual precipitating action is frequently taken advantage of by "topping" a basic colour with an acid one, or *vice versâ* by adding them separately and allowing them to react in the beater.

By this means the pulp is coloured more evenly, especially with mixtures of mechanical and chemical pulp. Solutions of the dyes should not be made sooner than they are required, as many of them decompose and form precipitates on standing in contact with the air. The solutions should be filtered through a wire-cloth to prevent any undissolved particles getting into the pulp.

There are a number of British firms who make a speciality of the manufacture of coal-tar colours for paper-makers. I give below a list of dyes of different makes, with instructions for their application, based on information furnished me by the firms in question :—

COAL-TAR DYES FOR PAPER PULP MANUFACTURED BY LEVINSTEIN, LTD., OF BLACKLEY, MANCHESTER.[1]

ACID COLOURS.—The acid colours are extensively used for colouring all classes of sized papers. For unsized papers, *e.g.* blotting papers, and in cases where the colour is required to withstand the action of water and steaming, colours of this class are unsuitable.

In dying with acid colours, the dyestuffs are dissolved in boiling water and added to the pulp previous to sizing. In many cases fuller and brighter shades are obtained by the use of an amount of alum slightly in excess of that required for sizing.

List of Acid Colours Suitable for Dyeing Sized Papers in the Beater.

Metanil yellow.[2]
Napthol yellow FYAS (preferably with addition of barium chloride).
Orange II.
Orange 4GB.
Blackley scarlet, extra conc.
Blackley fast scarlet.
Croceine Scarlet.
Fast red A.
Alkali blue brands.
Blackley blue DC.
Nigrosine (all brands).
Coomassie blue black.
Ochre buff, 6253 K, 6257 K.

---

[1] This firm is now amalgamated with British Dyes, Ltd.

[2] Excess of alum tends to turn Metanil yellow a brownish shade.

Substantive Colours.—The substantive colours are used, alone or in combination with acid colours, for colouring sized pulp. They are further adapted, and largely employed, for dyeing blotting and other unsized papers, and for the production of mottled papers, giving results characterised by good fastness to water. The backwaters are generally clear. The fastness to light is in some cases improved by an addition of copper sulphate to the dyed pulp. Colours sensitive to acids require an addition after dyeing of 3-4 lb. soda ash per 100 lb. weight of dry pulp.

List of Substantive Colours Suitable for Paper-Dyeing.

Dianol fast yellow ARX.
,, ,, orange G.
Vesuvine orange R.
Congo orange R.
Dianol orange D.
Congo red (with soda ash).
Benzo purpurine 4b, 10B (with soda ash).
Congo rubine.
Dianol fast red K, KN.
,, ,, claret 3B.
,, brilliant carmine B.
,, fast red F (dyed warm).
,, brilliant violet 2R.
,, violet N, R, O.
,, brilliant blue 6B (copper sulphate).
,, sky blue.
,, blue BX.
,, fast blue 2B.
,, green G, B.
,, brown LF, GM.
Crumpsall direct fast brown O, B.
Dianol black EX, RWX.
,, brilliant black BX.

Basic Colours.—Dyestuffs of this class are used both on sized and unsized pulps, and are characterised generally by their bright shades and great tinctorial power. An addition of tannic acid after dyeing improves the fastness to water in medium and dark shades. The basic colours are used both alone and in combination with dyestuffs of the acid and substantive groups. The following are suitable products :—

Magenta brands.
Phosphine brands.
Chrysoidine.
Bismarck brown.
Methylene blue.
Iodine blue brands.

Sulphide Colours.—Whilst the shades obtained with colours of this group are generally duller than those given by the preceding classes, the dyeings are distinguished by a high degree of resistance to the action of light, water, rubbing, alkalies and acids. The dyestuffs are insoluble in water but dissolve readily in boiling water when mixed with an equal weight of sodium sulphide.

The sulphide colours may be dyed both on unsized and sized pulps, but in the latter case the sizing is carried out only after washing the dyed material.

List of Suitable Sulphide Colours.

Thionol yellow, G, R.
,, orange L.
,, brown G conc., O, R, 2R.
,, black-brown G.
,, brilliant green 4GX.
,, green 3B.
,, corinth GX.
,, blue 2B conc.
,, black GSX conc., OG, etc.

List of Acid and Basic Colours Suitable for Staining Finished Papers.

Acid Colours.

Naphthol yellow YYAS.
Metanil yellow.
Vale yellow R.
Orange 4GB.
Blackley scarlet extra conc.
,, fast scarlet.
Croceine scarlet.
Double brilliant scarlet SX.
Azo eosine.
,, geranine B.
Napthol green G.
Blackley blue DC.
Nigrosine brands.

Basic Colours.

Bismarck brown—all brands.
Methylene blue.
Magenta.

Claus & Co., Ltd., of Clayton, Manchester.

This firm manufacture pure soluble blue, also duranthrene blue R.S. and G.C.D. These latter dyes correspond to the indanthrene blues, previously imported. The duranthrene blue R.S. is of a reddish shade. These dyes are insoluble in water and are usually supplied as a paste. They take the place of ultramarine for toning white papers, are stated to be equally permanent to light, and are not sensitive to excess of alum in the same way as many ultramarine brands.

Another English vat colour is carbazone blue which corresponds to hydron blue, previously imported. This is a vat colour of superior fastness to light to indigo.

Coal-tar Dyes Manufactured by British Dyes, Ltd., of Huddersfield.

Colours for Different Classes of Pulp.

Series 1.—*For Mechanical Pulp.*

1. Auramine O. II.
2. Bismarck brown R.
3. Magenta F.A.
4. Methyl violet 2B.
5. Malachite green crystals A.
6. Soluble blue 3M.

Series 2.—*For Unbleached Chemical Pulp.*

1. Auramine O. II.
2. Bismarck brown R.
3. Magenta F.A.
4. Methyl violet 2B.
5. Malachite green crystals A.
6. Soluble blue 3M.
7. Basic black.
8. Orange S.

Series 3.—*For Bleached Chemical Pulp.*

1. Auramine O. II.
2. Bismarck brown R.
3. Magenta F.A.
4. Methyl violet 2B.
5. Malachite green crystals A.
6. Soluble blue 3M.
7. Orange S.
8. Nigrosine crystals.

Series 4.—For Rag Papers.

1. Auramine O. II.
2. Bismarck brown R.
3. Magenta F.A.
4. Methyl violet 2B.
5. Malachite green crystals A.
6. Soluble blue 3M.
7. Orange S.
8. Nigrosine crystals.

Series 5.—For Brown Papers and Wrappings.

1. Auramine O. II.
2. Magenta F.A.
3. Bismarck brown.
4. Methyl violet 2B.
5. Malachite green crystals A.
6. Basic black.
7. Orange S.

Series 6.—For Blottings.

1. Chlorazol fast yellow N.T.
2. Chlorazol brown G.
3. Chlorazol violet.
4. Chlorazol blue B.
5. Chlorazol green B.
6. Chlorazol black E.

A more complete list of the dyes made by this firm is as follows:—

BASIC.

Auramine.
Azure blue B, 4R.
Bismarck brown R, Y.
Green powder A.
Chrysoidines.
Magenta, red shade.
Magenta, blue shade.
Crimson Y.
Methylene blues.
Brilliant green crystals Y.
Malachite green crystals A.
Green P.
Safranines.
Jute black MB conc.
Jet black B63846.
Green 67576.
Green 67577.

ACID.

Acid yellow FY.
Metanil yellows.
Quinoline yellow.
Indian yellow J.
Orange G, 2R.
Scarlet 2RJ, 3RD.
Croceine scarlets.
Cardinal reds.
Pink, B.M.
Bordeaux B.
Acid violets.
Tartrazine prima.
Acid green 2G.
Brilliant milling green S.
XL. Green Y.
Resorcine brown A.
Paper brown 66677.
Acid brown B, R.
Paper blue 65561.
Paper blue 69054.
Paper blue 69055.
Paper blue 69056.
Paper brown 67473.
Nigrosines.
Indulines.
Naphthalene blacks.
Alkali blues.

DIRECT.

Titan blacks.
Chlorazol blacks.
Chlorazol blues 6G, R.
Chlorazol dark blue B extra, R extra.
Chlorazol drab RH.
Chlorazol fast blue RH.
Chlorazol bright green 67918.
Chlorazol dark green 67914.
Chlorazol leaf green 67922.
Benzopurpurines.
Chlorazol fast red 10B.
Chlorazol red A.
Chlorazol red 8BS.
Paper red 69052.
Chlorazol blue 6BD100.
Chlorazol sky blue FF, FFS.
Chlorazol brown G, M.
Chlorazol catechin B.
Chlorazol brown 68042.
Reddish brown 67464.
Chlorazol green G.
Paper scarlet 69053.
Sultan scarlet 3B, F.
Chlorazol violet R, B.
Chlorazol fast yellow A, B, BS, FF.
Chlorazol yellow G.
Sultan yellow G.
Sun yellow G.

SULPHUR.

Cross dye brown D, 2D, 4R, 6R, 8R.
Cross dye yellows.
Cross dye drab.
Cross dye green B, F conc., D conc., G conc., I.
Cross dye blacks.
Cross dye blue FF conc., FR conc., D conc., G. conc.
Cross dye sky blue 3B conc.

ACID COLOURS are rather weak in colouring power on paper pulp, although they are more soluble than the basic colours, but they are faster to light and give level dyeings when fixed by the size. Tannin and metallic mordants are practically useless with this class of dyes. The solution of the dye must be mixed with the pulp before any sizing material is added. This is the essential condition for pulp-dyeing with acid colouring matters, and heavy subsequent sizing is essential for the production of deep shades.

Paper pulp dyed with acid colours is liable to give a finished paper with differently coloured sides. This difference is due to the action of the heat of the drying cylinders, and does not occur with basic colours. Hence when papers have been dyed with acid colouring matters. the drying cylinders must not be too hot.

Basic colours require a mordant with paper as in textile dyeing, and this is done by the addition of alum as used for sizing. Alum is usually quite sufficient for mordanting basic colours. At the same time they are fairly well fixed by china clay and fibres generally if the basic colour is added to the loaded pulp after it has been heated to a temperature of at least 140° F. but not exceeding 160° F. Another point with regard to level dyeing of paper with basic colours is that the dye solution should be well diluted with water before adding to the pulp. Basic colours possess greater colouring power than acid colours, but they are deficient in fastness to light.

Much better results are obtained by using both classes of colour, adding a basic colour to the pulp first and then an acid colour, towards which the basic colour first employed acts as a mordant.

Direct cotton colours are now used for all better class dyed papers, being fast to light under normal conditions and also producing very warm shades. They are largely used for blottings and in the production of mottled or ingrain fibre effects. The addition of Glauber's salt (sodium sulphate) is very beneficial to the dyeing operation and tends to fix the colour on the pulp. The addition of size and alum should always be made as late as possible after the addition of the colour.

There can be no doubt that the sulphur colours are destined to have a great future in paper-dyeing, but so far they are not used to any great extent by the papermaker. The difficulty lies in the necessity to use sodium sulphide to dissolve the colour. The method of dyeing is to add the colour dissolved in the sulphide solution to the pulp in the beater and run for about 1 hour ; then from ¼-½ per cent. sodium bichromate may be added on the weight of pulp in the beater. This is recommended for oxidising the sulphide during the constant beating action, and the pulp can be finished with size and alum. The object is to avoid the offensive smell and the action of the sulphide on the various metallic parts of the machine. It is reasonably certain that the great benefits which have accrued to textile dyeing by the introduction of sulphur colours will, before long, be realised in paper-dyeing.

The other dyes are best dissolved by pouring over them from 15 to 20 times the quantity of boiling water, stirring all the time. An exception to this rule is auramine with which water at a higher temperature than 140° F. must not be used.

All the acid colours require an excess of alum ; this is particularly the case with the various brands of soluble blue. The following colours are fixed better and give brighter shades with an additional quantity of alum (4-5 lb. per 100 lb. paper):—

Soluble blue 3M.
Nigrosine.

On the other hand, an excess of alum must be avoided with all dyes of the eosine group, and the substantive dyes.

An addition of 5-15 lb. aluminium acetate solution (14 Tw.) per 100 lb. of paper is advantageously made when using orange, especially with heavy shades. An addition of 2-4 lb. of borax per 100 lb. of paper is advantageously made with the following colours mentioned below:—

Diamond magenta.
Auramine O. II.
Methyl violet 2B.
Victoria blue.
Malachite green crystals A.

NOTES ON DYEING WITH COAL-TAR COLOURS.

(*a*) *Dyeing with Basic Colours.*—Add to the paper pulp in the beater 2·4 per cent. sulphate of alumina dissolved in water, allow to run for several minutes, and then add the basic colour thoroughly dissolved in water. Allow to run for 10 minutes and then add 4 per cent. rosin size dissolved in water (obtained by saponifying 1 lb. colophony with 4 oz. soda in 1 gallon water).

When dyeing with combinations of colours, add the several colours to the paper pulp one after the other.

The back-water is generally clear in about a quarter of an hour.

(*b*) *Dyeing with Acid Colours.*—Acid colours are dyed in a similar manner to basic dye stuffs by adding 4 per cent. sulphate of alumina dissolved in water to the paper pulp, then the dissolved acid colour, and afterwards the rosin soap.

Basic or acid colours used for staining purposes are thoroughly dissolved in water and the colour solution carefully filtered before applying to the paper.

Tissue paper is dyed in the machine by running the web through the concentrated colour solution, and then over drying cylinders.

When dyeing combinations, care must be taken to select colours that do not precipitate one another.

For saddening blue shades produced with combinations of violet and green, metanil yellow or vesuvine may be used.

ESTIMATION OF MOISTURE IN PULP.

Mechanical and chemical wood pulp has more frequently to be dealt with than any other form of half-stuff, although rag, esparto and straw pulps are also met with.

Tests are made with a view to determining the percentage of air-dry pulp in the consignment. All air-dry fibrous materials hold a small proportion of moisture, which will vary with the kind of fibre and also with the atmospheric conditions—that is, the temperature and percentage of moisture in the atmosphere (humidity).

The table below gives the percentage moisture contained in the various half-stuffs when exposed in loose heaps to air of varying degrees of humidity :—

TABLE LXIII.

PERCENTAGE MOISTURE IN HALFSTUFFS.

Relative Humidity of the Air.	Per Cent. Moisture contained in				
	Cotton Half-stuff.	Linen Half-stuff.	Chemical Soda. Pulp.	Brown Mechanical Pulp.	Mechanical Pulp.
40	4·9	5·3	5·8	6·4	8·0
50	5·4	6·0	6·6	7·2	8·8
60	5·7	6·3	7·4	8·0	9·4
70	6·1	6·8	8·4	8·8	10·0
80	6·8	7·7	9·6	9·9	10·6
90	8·0	9·5	11·3	11·5	12·0

The relative humidity or percentage saturation is expressed as a percentage of that due to a state of saturation at the temperature. The higher the temperature the greater the amount of moisture required to saturate a given volume of air, so that the higher the temperature the lower the relative humidity for air containing the same percentage of water vapour.

It is necessary for commercial purposes to arrive at some figure for the percentage of moisture in air-dry pulp which is taken as a basis for reckoning. The figure, arbitrarily chosen, only roughly approximates to the experimental figure. In Great Britain the moisture in air-dry pulp is reckoned at 10 per cent. for all fibrous material. That is—

In Great Britain . 100 parts air-dry = 90 parts bone-dry + 10 parts water.
In France . . 110 ,, ,, = 100 ,, ,, + 10 ,, ,,
In North Germany 100 ,, ,, = 88 ,, ,, + 12 ,, ,,
In South ,, 112 ,, ,, = 100 ,, ,, + 12 ,, ,,

"Moist" mechanical or chemical pulp is reckoned half moisture and half air-dry pulp, that is—

100 parts moist pulp = 50 parts air-dry = 45 parts bone-dry.

The estimation of moisture consists of—(1) Sampling, that is, the removal of a fair sample representative of the whole consignment; (2) moisture estimation, that is, the determination of the percentage of absolutely dry (bone-dry) pulp in the sample. From the weight of the bales taken for sampling and percentage of bone-dry pulp the weight of air-dry (or moist) pulp in the whole consignment is calculated.

(1) *Sampling—Selection of Bales.*—Not less than 2 per cent. or more than 4 per cent. of the total number of bales are taken for sampling, according to the size of the consignment and discretion of analyst. If the bales are numbered, consecutive numbers should be avoided, as the sample bales should be taken from all parts of the stock as far as possible. The bales chosen should be "intact," they should not be damaged through the wires being broken or corners knocked off. Abnormally heavy bales should be rejected if they show signs of having been wetted by exposure—in my opinion, there is no reason for rejecting bales merely because they are heavy, as pulp mills do not exercise great care in making up bales to the same uniform weight. The essential requirement to keep in view is the selection of bales representative of the whole.

Weighing.—Bales may weigh 1 to 4 cwt. If the weighing machine will take several bales at a time, several may be weighed together, as the error in weighing will be smaller than if the bales be weighed singly, and time will be saved, especially when sampling large consignments.

Removing Sheets and Cutting Samples.—A number of sheets, usually three to five, are removed from each bale, as it is impossible to sample all sheets, and these sheets should be representative of the whole bale. As the outer sheets will differ most from the bulk if the bale has been exposed to abnormal conditions, such as rain or sun, most analysts recommend that sheets should be removed at a point within about 1½ in. of either end of the bale. These sheets may be regarded as representative of the first 3 inches at the top and bottom of the bale. As, however, it is impracticable to remove one sheet for every 3 inches depth of bale, smaller samples must be cut from the two outer sheets than from those taken from the inner portion of the bale. Supposing the depth of the bale (sheets piled upon one another) be 33 inches and three sheets be selected from each bale—two outer sheets and one from the middle. Each outer sheet will be representative of 3 inches depth of sheets, and the middle of sheet of 27 inches, therefore nine times as much pulp must be removed from the middle sheet as from each of the two outer ones. The sheets selected from each bale should be, as far as possible, of the same thickness.

There are several methods of cutting samples from the sheets. It has been shown that the mathematically correct method of cutting a sample in order to include the right proportion of the inner and outer portions of the sheet is to cut a wedge having the middle of the sheet as the apex and the edge as the base of the triangle. Taking the example given above, of a bale 33 inches deep, if a wedge is cut from the outer sheets having a ½ inch base, the wedge from the middle sheet would have a 4½ inch base. If possible, four wedges are cut from each sheet, one wedge from each side, but where a large number of bales are to be sampled one or two wedges only can be cut from each sheet. The analyst uses his discretion and is guided by circumstances.

Many analysts recommend taking five sheets from each bale, and this should be done if possible, the size of the sample taken from each sheet being proportional to the depth of the bale which it is intended to represent.

It is objected on some sides that it is difficult to cut wedges rapidly to any particular size, and the cutting of cross or diagonal strips or pieces from different parts of the sheet is recommended, and applied in practice.

In the case of some moist mechanical pulp, where it is next to impossible to select sheets of the same thickness, it is very difficult to cut samples of any particular size from the sheet. In such cases the more empirical methods, much used in practice, are as likely to give correct results as any other. Five sheets are taken evenly distributed throughout the bale, the top and bottom sheets being within 1½ in. of the ends of the bale. Small samples are removed from the middle and at points halfway towards the corner of the sheets, making five pieces from each sheet and twenty-five pieces from the bale. With moist pulp they need not be cut out, but picked out with the point of the knife and the thumb, which can be done very quickly indeed.[1]

In 1908 a method of sampling devised by A. Bowman was officially adopted by the committee on wood pulp testing. This is a wedge system, the wedges being cut to a definite size by means of a special templet graduated for the purpose. The five sheets from each bale are selected at equal distances apart, but in different positions for each of six bales taken. The method is, comparatively speaking, complex, and sampling takes longer than by the other methods described. For details the reader is referred to R. W. Sindall's paper in the *Paper Trade Review*, Nos. 14 and 16 of volume 50, or *The Testing of Wood Pulp*, by Sindall and Bacon, pp. 21-25.

The samples, as soon as cut, should be placed in air-tight lever-top tins or jars, which should be kept covered, or, if they are to be weighed at once, may be placed between a folded sheet of pulp.

(2) *Determination of Moisture.*—If the samples are not weighed at once they are removed in air-tight vessels, which are weighed before emptying and again after emptying: the difference will be the weight of pulp in the tin. The pulp may be reweighed as a check, as one error in weighing will destroy the validity of the whole test. When the pulp is more than sufficient to fill one tin, I make it a practice to dry the contents of each tin separately, so as to be able to compare the percentage of moisture in each lot of pulp. The balance should be sufficiently sensitive to weigh to 1 decigram. The pulp is

---

[1] For further details the following may be consulted: Sindall, *The Sampling of Wood Pulp;* Lester, *Paper and Pulp*, 15th April, 1902, p. 291—15th March, 1905, p. 183; Winkler, reprint in pamphlet form from *Paper and Pulp*, 1905—this translation was made by myself from the original German in order to show what views are held on the Continent; Sindall and Bacon, *The Testing of Wood Pulp*, 1912.

placed in small baskets or cages of wire gauze, which fit the oven, which may be heated by steam or hot air; in the latter case, the oven should be provided with a thermometer and the temperature maintained at 100-110° C. Although the temperature of a steam- or water-oven may be a trifle under 100° C., I have not found that pulp dried in such ovens loses appreciably further in weight when transferred to a hot-air oven at 100-110° C. When the pulp is nearly dry it should be weighed every half-hour, as the dry pulp gradually increases in weight from oxidation in the air. The pulp is either weighed in the cage immediately on removal from the oven, or may be emptied into a lever-top tin, which is immediately shut down and weighed when cold. In either case the weight of the cage or tin must, of course, be deducted to obtain the weight of the bone-dry pulp. I have satisfied myself that no appreciable error is introduced by weighing the pulp while still hot, on the first method. Ovens are also built with balance attached so that the weight of the pulp may be taken at any moment without removing it from the oven.

Calculation.—Let A be the weight of the pulp as sampled, and B the weight of the bone-dry pulp, then $\frac{B}{A} \times 100 = X =$ the percentage of bone-dry pulp in the sample, and $100 - X =$ percentage of moisture in the sample. Further, $\frac{10}{9} X = Q =$ percentage of air-dry ($90 = 100$) pulp in the sample. If this figure is less than 100 the difference between it and 100 will represent excess moisture in the pulp, but if greater than 100, the difference will represent the excess air-dry pulp in the sample. Of course if the consignment consists of moist ($45 = 100$) instead of air-dry pulp, $Q = \frac{100}{45} X$.

Let P be the percentage of bales sampled, and W be their weight, then $W \times \frac{100}{P} = T =$ total weight of consignment and $T \times Q$, that is, the total weight of consignment multiplied by the percentage of air-dry pulp contained therein = the total weight of *air-dry* pulp in the consignment.

I append a certificate giving a report on a consignment of chemical pulp tested for moisture:—

WOOD PULP MOISTURE CERTIFICATE.

(Form adopted by the British Wood Pulp Association.)

This is to Certify that I have tested for moisture a parcel of Dry Sulphite Pulp, said to consist of 600 bales, marked Balta, ex. S.S. *Andromeda*, lying at Messrs. the X. Paper Mills Co. The samples were drawn by us on 5th June, 1917.

	Bales.	T.	cwt.	qrs.	lb.
Total gross weight of bales sampled (intact) ***(For numbers and detailed weights see below.)***	24	4	0	0	22
Weight of parcel calculated from above .	600	100	4	3	18

Percentage of absolutely dry pulp in the sample .	85·33 per cent.
„ moisture in the sample . . .	14·67 „
„ air-dry or moist pulp in the parcel on the basis of 90 = 100 (air-dry) . .	94·81 „
45 = 100 (moist) . .	
„ excess moisture	5·19 „

	T.	cwt.	qrs.	lb.
Weight of pulp to be invoiced	95	0	3	12

NUMBERS AND DETAILED WEIGHTS OF BALES SAMPLED.

No. on Bales.	Cwts.	Qrs.	Lb.	No. on Bales.	Cwts.	Qrs.	Lb.
					40	0	2
13741	3	1	15	12576	3	1	14
13254	3	0	27	11438	3	1	25
12351	3	1	18	10986	3	1	12
11571	3	1	11	11321	3	1	17
12315	3	1	4	11963	3	1	0
12413	3	0	26	11841	3	0	25
11326	3	1	18	12457	3	1	7
12437	3	1	15	11375	3	1	16
13361	3	0	21	13336	3	1	26
12329	3	1	8	13291	3	1	3
11315	3	1	19	13145	3	1	10
12412	3	1	16	12397	3	1	5
	40	0	2		80	0	22

(Signed) HENRY P. STEVENS, Analyst.

CHAPTER VII.

PAPER ANALYSIS AND PAPER TESTING.

Examination of Paper.—The properties of a sheet of paper are largely conditioned by the properties of the fibres of which it is composed, in particular by the length, breadth, flexibility, general form, nature of surface, size of canal or "lumen" and thickness of walls, and also by the changes the fibre undergoes in beating. In the latter operation much depends on whether the fibre readily splits into fibrillæ, thereby increasing the felting qualities and possibly also the strength of the paper.

A microscopic examination of fibres yields information on these points, and is not only of value for the purpose of identifying the particular fibres of which the paper is composed, but also for the purpose of ascertaining in a general manner the treatment to which the fibres have been subjected. When the paper is composed of more than one kind of fibre a microscopic examination enables an estimate to be formed of the proportions in which the fibres are present.

General Properties of Fibres.—The length and breadth of fibres are given in the accompanying table. The actual strength of the ultimate fibre is of hardly so great importance as its felting qualities. When a paper is torn it is rather a question of pulling the fibres apart than of rupturing them.

TABLE LXIV.

AVERAGE DIMENSIONS OF FIBRES.

	Length. Mm.	Breadth. Mm.
Cotton	30	·025
Linen	25	·020
Hemp	20	·022

TABLE LXIV (*continued*).

	Length. Mm.	Breadth. Mm.
Jute	2·5	·022
Esparto	1·5	·012
Straw	1·5	·015
Wood (coniferous trees)	3	·030
,, (deciduous trees)	1	·020
Manilla	7	·020
Sunn hemp	8	·030
New Zealand flax	8	·015
China grass	22	·050
Ramie	150	·050
Adansonia	12	·020
Bamboo	4	·015
Paper mulberry or Kodsu (*Broussonetia papyrifera*)	12	·025
Mitsumata (*Edgeworthia papyrifera*)	3	·010
Lygæum spartum	2·5	·015
"Banana" (*Musa paradisaica*)	5	·030
Sugar cane (bagasse)	3	·015
Cocoanut fibre	1·5	·012
Hedychium coronarium	2·6	

TABLE LXV.

INCREASE IN LENGTH OF FIBRE OF *Pinus sylvestris* WITH AGE AS MEASURED BY NUMBER OF ANNUAL RING (GOODALE).

No. of the Annual Ring.	Medium Length of the Tracheids. Mm.	Medium Width of the Tracheids. Mm.
1	0·95	0·017
17	2·74	—
19	3·13	—
31	3·69	—
37	3·87	—
38	3·91	—
39	4·00	—
43	4·09	—
45	4·21	—
46	4·21	—
72	4·21	0·032

It will be noted that the length of the fibre increases up to the 45th year, after which it remains constant.

The following table gives the measurements of the fibres of a large number of pulps prepared by Surface :—

TABLE LXVI.

AVERAGE LENGTH OF FIBRES (BEADLE AND STEVENS).

	Mm.
Red maple	0·78
Aspen	0·98
Red alder	1·08
Beech	1·18
Bald cypress	1·34
Tulip tree	1·54
Sycamore	1·65
Cotton gum	1·66
Engelmann spruce	2·31
Hemlock	2·36
Incense cedar	2·41
Jack pine	2·41
Lodgepole pine	2·50
Tamarack	2·61
Western hemlock	2·62
Red spruce	2·76
Loblolly pine	2·86
Scrub pine	2·90
Grand fir	3·13
Douglas fir	3·32
White fir	4·02
Longleaf pine	4·28

According to this table, the average length of fibre of the hard (deciduous) woods is 1·22 mm., and of the coniferous woods 2·56 mm.

Special attention may be drawn to the fibres of the Southern pine or Longleaf pine (*Pinus palustris*, Mill), which grows plentifully in the southern states of the United States. According to the above figures the fibre averages 4·28 mm. in length, but measurements made on another sample of the raw material gave an average figure of 5·28 mm.[1]

The specific gravity of most paper-making fibres approximates to 1·5 ; the most notable exception is mechanical wood, whose specific gravity is about 1·1. The accompanying table gives the specific gravities of some of the more important animal and vegetable fibres :—

---

[1] Beadle and Stevens, *Chem. News*, 1915, p. 225.

TABLE LXVII.

SPECIFIC GRAVITY OF FIBRES.

(Matthews.)

Cotton	1·50 to 1·55
Linen	1·50
Hemp	1·48
Jute	1·48
Ramie	1·51 to 1·52
Wool	1·28 to 1·33
Mohair	1·30
Silk, raw	1·30 to 1·37
,, boiled off	1·25

(Müller.)

Chemical wood	1·43
Mechanical wood	1·12

All fibres contain a certain amount of hygroscopic moisture depending on the amount of moisture contained in the atmosphere to which they are exposed (see also *Estimation of Moisture in Pulp*). The accompanying table gives the amount of moisture held by fibres in the air-dry condition, and also the greatest amount they will absorb hygroscopically :—

TABLE LXVIII.

HYGROSCOPIC MOISTURE IN FIBRES (WIESNER).

	Fibre Air-Dry.	Fibre with the Maximum Amount of Hygroscopic Moisture.
Cotton	6·66	20·99
Flax	5·70	13·90
Jute	6·00	23·30
Esparto	6·95	13·32
China grass	6·52	18·15
Manila hemp	12·50	40·00
Sunn hemp	5·31	10·87

Although vegetable fibres consist chiefly of cellulose they contain, in addition, mineral matter, and foreign vegetable and albuminous matters, etc. The mineral matter contained in fibres is small, the ash averaging about 1 per cent. The accompanying table gives the ash in a number of fibres. The figure, of course, will depend largely on the extent to which the fibre has been treated in separating it from foreign matter. Thus the figure for jute will vary between 2·8 and ·7, according to the quality of the fibre.

TABLE LXIX.

Ash of Fibres.

(Mostly after Müller.)

Cotton	0·12
Hemp (Italian)	0·82
Manila hemp	1·02
Sunn "	·61
Ramie	5·63
China grass	2·87
Jute	1·32
" (Matthews)	·68
New Zealand flax	0·63
Esparto	3·50-5·04
Adansonia	4·72-6·19
Sulphite pulp fibre (Frank)	0·46-2·60
Soda " " "	1·00-2·50

Mechanical wood contains the greater part of the ligneous, albuminous and encrusting matters of the original wood. Even cotton in the raw state is by no means pure cellulose, as will be seen from the accompanying analysis :—

TABLE LXX.

Composition of the Cotton Fibre.

Cellulose	83·71
Proteids	1·50
Nitrogen free extract	5·79
Fat	0·61
Water	6·74
Ash	1·65

Analyses by Church and Müller show 91·15-91·35 per cent. cellulose and 0·11 to 0·12 per cent. ash.

Botanical Source of Fibres.—The greater number of paper-making fibres may be included in the following three categories :—

(1) Seed hairs, of which cotton is the representative.

(2) Bast fibres, from the bark and stems of plants, of which flax, hemp, jute and the greater number of paper-making fibres consist.

(3) Vascular fibres, mostly from the leaf tissues, of which New Zealand flax is an example.

(4) Tracheids and other fibres from wood.

The seed hair cotton is of great length (20 to 40 mm.). One end only is pointed, the other being attached to the seed. As a general rule, the walls are thin and the central canal large, so that when dry the fibre often collapses to a sort of ribbon and at the same time acquires a peculiar and characteristic twist.

The bast fibres are shorter and have thicker walls. In sections they are rounded or polygonal. They are pointed at both ends.

In many cases, as in flax and jute, numerous fibres are attached together to form a filament which is comparable in length with the cotton fibre. When boiled and bleached these filaments become separated into their ultimate fibres.

Wood-pulp fibres from coniferous trees (pine, fir, spruce, etc.) consist mostly of tracheids, which are characterised by numerous pores having the appearance of disc-shaped markings. Pulp from deciduous trees (poplar, aspen birch, etc.) consists chiefly of true wood fibres, shorter than the tracheids of the coniferous trees, together with short wide cells with disc-shaped markings.

Microscopic Examination of Fibres.

Preparation of Sample for Analysis.—If the material for examination consists of pulp or paper which is unsized or soft-sized, a small portion may be removed by moistening the sheet and scraping the surface with a spatula or blunt blade of a knife. If the paper is hard-sized but not tub-sized, a small piece is heated in an evaporating dish with a 1 per cent. solution of soda for ten minutes or so, and after well washing with water by decantation, is transferred to a strong glass-stoppered bottle of 200 or 300 c.c. capacity.

Parchment papers cannot be disintegrated by boiling with soda, but sulphuric acid diluted with its own volume of water may be used instead. The acid is warmed to

50°-60° C. and a small piece of the paper immersed and stirred in with a glass rod. In 2-5 minutes the paper should be sufficiently disintegrated and the whole is poured on to a piece of machine wire and the fibre well washed with water. Papers which have been sized with viscose exhibit great resistance to disintegration and are not resolved by either alkali or acid, for the reason that the regenerated cellulose (from viscose) binds the fibres together. The sample for examination must be scraped from the sheet with a knife.

If the paper be tub-sized, it is boiled with water alone and washed, previous to treating with soda, in order to remove the gelatine. Coated papers should be treated in a similar manner. The bottle containing the sample is filled with large glass beads or rough garnets to a depth of about half an inch, and water added. The stopper is then replaced and the bottle shaken vigorously (for five minutes or longer, if necessary) until the paper is completely reduced to fine pulp and the fibres separated from one another by the friction of the beads. If the paper is unsized or very soft-sized, it may be reduced to the necessary condition of pulp without the use of beads. The water with the fibres in suspension is poured off through a piece of fine-mesh machine wire. It is important that the whole of the fibre should be transferred, or the sample of pulp will not be representative of the sample of paper, as the finer fibres remain suspended in the water longer than the others and are poured off first. The pulp on the wire is washed with a little distilled water and is transferred to a test-tube or watch-glass for use. A speck of the pulp is placed on a microscope slide with the aid of a preparation needle—a pointed steel wire or large needle fixed in a wooden handle—spread evenly on the glass, and the fibres teased out with a glass rod and needle. A cover glass is placed in position, and the preparation is now ready for putting under the microscope for examination, unless it is to be stained or otherwise treated with special reagent. In any case, it is as well to make a preliminary examination of the fibre in an untreated state, first under a low power, and afterwards using a higher power and carefully examining characteristic fibres. Avoid high powers as far as possible. A conclusion should then be drawn as to the nature and identity of the fibres. The effect of the different stains and reagents described below is resorted to for the purpose of confirmation only or for judging the proportions in which the different fibrous constituents are present. The stains also bring out the characteristic structure and markings on the fibres.

Stains and Special Reagents.—These, if used with due care, are valuable aids to microscopic analysis, but the characteristic colours produced cannot be invariably relied on, as they are influenced by the condition of the fibre and the treatment it has undergone. The reagents must also be carefully prepared according to fixed receipts, and preserved in well-stoppered bottles.

Methylene Blue.—A solution of this dye is sometimes useful for the purpose of staining the fibres so that the latter stand out blue on a colourless background, but it does not serve any useful purpose for differentiating between different fibres, except to emphasise characteristic markings and striations. A drop is placed on the preparation before putting the cover glass in position.

Iodine in Potassium Iodide Solution.—This reagent is prepared according to the following receipt (Herzberg):—

Potassium iodide	2 grams.
Distilled water	20 c.c.
Iodine	1·15 grams.
Glycerine	2 c.c.

A drop of this solution is placed on the slide and a speck of pulp placed in it by means of a glass rod or stout platinum wire and teased out as already described. If an iron needle is used, it must be wiped immediately after use, as the metal is attacked by the iodine; this also applies to other iodine reagents. The cover glass is dropped on the top and the excess of iodine solution removed by applying a piece of filter paper to the edge of the cover glass. Care is taken to avoid the inclusion of air bubbles, although this is not of great importance in a preparation which is not of a permanent nature.

Treated in this manner:—

Rag, cotton, linen, and bleached hemp are coloured *brown.*

Chemical wood fibres, bleached straw and jute remain *colourless* or a *pale grey-brown.*

Mechanical wood, unbleached jute, straw, and ligneous fibres generally, are coloured *yellow* or *yellow-brown*, according to the amount of encrusting matters present. Esparto, Manila, and Adansonia are coloured *grey to brown.*

Iodine and Sulphuric Acid.—The fibre is treated with iodine in potassium iodide reagent as before, and after allowing to stand for a minute or two the excess of solution is mopped up with filter paper. Care is taken that no fibres are removed from the filter paper and left on the slide. The small portion of the brown pulp is now treated with a drop of sulphuric acid made by diluting 125 c.c. of the strongest acid with 100 c.c. water.

The following colours are developed (Höhnel) :—

Cotton, linen, and bleached jute are coloured *violet-red to wine-red.*

Chemical wood and straw fibres are coloured *blue to blue-grey.*

Mechanical wood, raw jute, and encrusted fibres are coloured *golden to dark yellow.*

Iodine and Zinc Chloride Reagent (Herzberg) is prepared by dissolving 20 grams dry zinc chloride in 10 c.c. water and adding to it a solution prepared by dissolving 2·1 grams potassium iodide and 0·1 gram iodine in 5 c c. water. The mixed solutions are allowed to stand and poured off from any sediment, and finally a crystal iodine is added to the clear solution.

The water is removed from the particle of pulp on the slide as completely as possibly with a piece of filter paper, and a drop of the reagent added.

Treated in this manner :—

Rag, cotton, linen, and hemp are coloured *wine-red* or *brownish-pink.*

Chemical wood fibres, bleached straw and jute are coloured *blue-violet.*

Mechanical wood, unbleached jute and straw, and ligneous fibres generally, are coloured *yellow.*

Straw at times takes a bluish shade ; esparto bluish or reddish ; Manila almost any shade from blue to yellow. Adansonia gives the same colour reactions as chemical wood.

Iodine and Magnesium Chloride Reagent (Jenke) is prepared by mixing 50 c.c. saturated magnesium chloride solution with 2·5 c.c. of a solution prepared by dissolving 23 grams potassium iodide and 1·5 grams iodine in 20 c.c.

water. The preparation is made in the same manner as when using the iodine and zinc chloride reagent.

Treated in this manner, the following colours are developed :—

Cotton, linen, and hemp are coloured *brown.*

Bleached straw fibres are coloured *blue-violet.*

Chemical wood fibres remain *colourless* or are coloured faintly reddish.

Mechanical wood fibres, unbleached jute, etc., are coloured *yellow.*

MICROSCOPIC CHARACTERISTICS OF FIBRES.

Cotton (fig. 37) has the general appearance of an irregularly flattened tube with numerous twists, which are very characteristic, although they are also occasionally met with in chemical wood fibres. The cotton fibre is very transparent, and the flattened portions frequently exhibit cross markings or striations resembling wrinkles or folds, while the edges present a raised and rounded appearance, as might be expected in a collapsed tube with a dumb-bell-shaped section. These characters are clearly seen in the illustration.

FIG. 37.—Cotton.

In the process of boiling rags and beating the half-stuff these characters are largely obliterated, and the fibres from a strong sheet of paper present a very different appearance. They are not only cut up into short lengths, but split and frayed to such an extent that many of them are no longer recognisable. A portion of the fibre is thus reduced to a shapeless mass, and the constituents of the paper as a whole can only be recognised from a small proportion of the fibres which have escaped drastic treatment. The characteristic structure is least altered in the case of free beaten stuff as required for the manufacture of blottings ; the fibres are here cut up into short lengths, and are otherwise but little altered. As the original fibres are long, the natural ends are seldom seen.

Linen (figs. 38 and 39).—Fig. 39 shows the fibres under higher magnification. In contrast to the cotton fibres the linen fibres are regularly rounded or polygonal, and possess a narrow canal or lumen of fairly uniform size throughout the length of the fibre. This canal is not always very apparent when the fibres are first examined. Whereas cotton fibres are thin walled, linen fibres possess thick walls, which at frequent intervals show thickenings resembling knots or joints, and transverse markings. As it is less flexible than the cotton fibre, it is generally straighter, with sharper bends. The fibres narrow down gradually, tapering to a fine point. The fibre also shows faint parallel markings. On the whole, it is transparent like cotton.

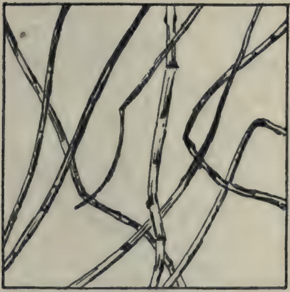


FIG. 38.—Linen.

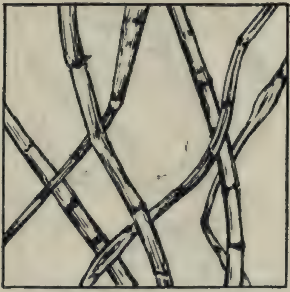


FIG. 39.—Linen (more highly magnified).

In paper-making operations the appearance of the fibre undergoes a very considerable change owing to the readiness with which it splits longitudinally; the fibres of a tub-sized loan or bank are either frayed at the ends and split into numerous fibrils or the fibre may be split completely from end to end. Other fibres are converted to a shapeless mass. Under less severe treatment the fibres are flattened, in places bulging out on both sides, but as the beating is continued short lengths are entirely flattened, taking on the appearance of cotton fibres. As a result it is often very difficult to state positively whether a paper produced from wet beaten rags should be classed as a cotton or linen paper, and next to impossible to estimate the proportions in which these fibres are present. It should, however, be remarked that no linen papers are entirely free from cotton fibres, and many *bonâ fide* linen papers made from linen cuttings will be found to contain as much as 50 per cent. of cotton. Unfortunately cotton and linen stain practically alike with the iodine preparations.

Hemp (fig. 40).—In general appearance the hemp fibre resembles the linen fibre. It shows similar thickenings resembling knots or joints, with transverse markings. The canal is perhaps a trifle larger, and there are numerous longitudinal markings. Further, numerous small hairs may be detected on the surface of the natural fibres at the knots or joints. The fibre ends are mostly blunt, and occasionally forked, in contrast to the tapering ends of the linen fibres. Generally speaking, the hemp fibres are more opaque than the latter. Although these characteristics may suffice to distinguish the two fibres in the form of half-stuff, it is very difficult to distinguish between them after treatment in the beating engine. Hemp, like linen, splits easily into fibrils, or down its whole length, so that the appearance of the two fibres is practically identical. Fortunately this is of minor importance to the papermaker, as linen and hemp lend similar properties to the paper into which they are made.

FIG. 40.—Hemp.

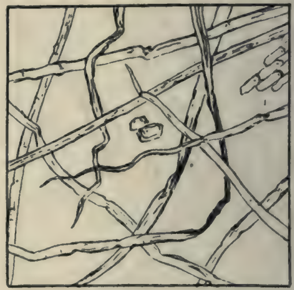


FIG. 41.—Manila.

Zinc chloride and iodine solution colour hemp a pinkish colour when freed from encrusting matter; the partially boiled and unbleached fibre, as used for insulating cable paper or strong browns, gives varying shades of colour approaching to yellow.

Manila or Manila hemp (fig. 41) differs considerably in appearance and properties from ordinary hemp. Whereas the latter is thick-walled, with a small canal, Manila is comparatively thin-walled, with a large canal; that is, the canal is three or four times as broad as the walls of the fibre. Speaking generally, the fibres, on casual inspection, resemble the tracheids of wood rather than bast fires of hemp, while in other respects they may be likened to jute fibres with large canals. The resemblance to jute is sometimes very marked; some Manila fibres have small canals, which vary in thickness but are never so narrow as in jute ordinarily. Irregularities on the surface of the jute fibre are more marked than in the case of Manila. The ends of the fibres taper off gradually to fine points. Accompanying the fibres are oblong-shaped cells, which may aid the identification of the fibre in paper.

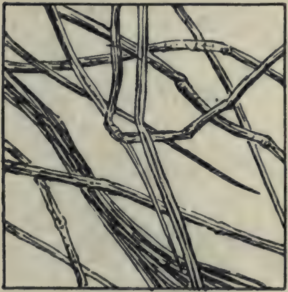


FIG. 42.—Jute.

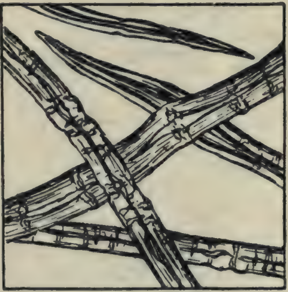


FIG. 43.—Jute (more highly magnified).

Jute (figs. 42 and 43).—This is a comparatively thick-walled fibre, the varying size of the canal being very characteristic. It resembles hemp or flax in general appearance, with striations parallel to the fibre, knots and transverse markings. The varying size of the canal is brought out in fig. 43, and also the extremity of the fibre, which sometimes broadens out into a somewhat spearshaped form, the canal being correspondingly broader at this point. Jute is a woody fibre, and except in the well-boiled and bleached conditions, gives the colour reactions of mechanical wood, including the bright yellow coloration, with iodine preparations.

Esparto (figs. 44 and 45).—The bast fibres are short and narrow, cylindrical in section, tapering off at the ends to fine points. The central canal is small. In addition to these there are other cells, characteristic and useful for purposes of identification, in particular the seed hairs or tiny comma-shaped cells, rounded at one end and tapering to a point at the other (figs. 44 and 45). Further, there are the serrated (epidermal) cells, seen on the right of fig. 45, the schlerenchymatous cells and pitted vessels on the left of the same illustration. It is noteworthy, however, that esparto contains none of the thin-walled parenchymatous cells found in straw (figs. 46 and 47). The esparto fibres are so small that to a large extent they escape the action of the beater knives, with the result that they are not much altered in the process of converting the half-stuff into paper.

FIG. 44.—Esparto.

FIG. 45.—Esparto (more highly magnified).

Straw (figs. 46 and 47).—Ordinary straw pulp contains a variety of cells. There are, firstly, the bast fibres, in which the thickness of the walls and size of canal vary considerably. The ends of these fibres taper gradually to fine points and the body of the fibre shows frequent kinks and bends. Secondly, there are the thin-walled, oblong, parenchymatous cells; two of these are seen hanging together at the top left-hand corner of fig. 47. These are so frail and transparent that they are easily missed in an unstained preparation. Thirdly, the serrated epidermal cells (top right-hand corner, fig. 47). Also schlerenchymatous cells, pitted vessels, etc. Straw pulps of different origin strongly resemble one another. The chief distinguishing characteristics of different straws are to be observed in the serrated epidermal cells.

FIG. 46.—Straw.

FIG. 47.—Straw (more highly magnified).

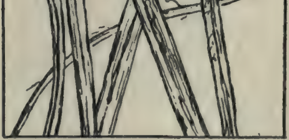


FIG. 48.—Ramie.

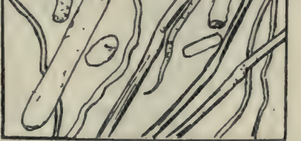


FIG. 49.—Bamboo.

Ramie fibres are thick-walled, with narrow canal (fig. 48).

Bamboo (fig. 49).—The fibres somewhat resemble those of straw. They usually taper to fine points. Oblong and rounded cells are common.

Wood Pulp.—The cells from different trees present somewhat different structures, but those from the conifers, such as pine, spruce, fir, hemlock, balsam, etc., closely resemble one another (figs. 50-52). On the other hand, the cells of deciduous trees, such as poplar (fig. 53), aspen, etc., have characteristics which differentiate them from the conifers. The paper-making fibre obtained from conifers consists mostly of those cells known as tracheids; they are transparent and thin-walled, although the canal varies considerably in size. The surface of many cells shows characteristic pits, on which appear small circular or elliptical openings. These are most frequent in the cells formed in the early part of the year, when the fibres are broader and have a wider canal than the cells of the wood formed later on in the year. These broad fibres sometimes appear like ribands, showing twists and folds of a similar character to the cotton fibre, but the former are easily distinguished by the pits on the surface or by the fact that they are stained blue with zinc chloride and iodine solution.

FIG. 50.—Chemical Wood Pulp (Hemlock).

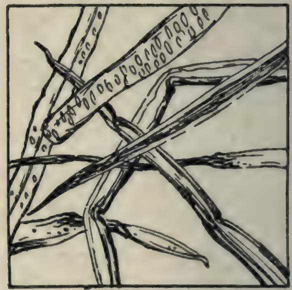


FIG. 51.—Chemical Wood Pulp (Hemlock), (more highly magnified).

The paper-making fibres of the deciduous trees, such as poplar and aspen, consist of the true wood fibres or libriform cells. They are shorter than the tracheids of the conifers, the canals are uniformly larger and show occasional pits and similar markings, usually oval in form.

In addition there are numerous large pitted vessels. Two of these are shown in fig. 53. The markings on these cells differ according to the species, and serve to identify the wood from which the pulp has been made. Mechanical wood pulp (fig. 54), consisting as it does merely of ground particles of wood, presents no difficulties in the way of identification. The particles are of every size, from torn pieces of fibres to clumps of fibres hanging together, which may be large enough to be detected by the naked eye—say ·25 mm. or more. The proportion of large to small particles will show to what extent the pulp has been ground; in the finest ground pulp the fibres are split lengthways and are therefore narrower than the fibre of chemical wood. A careful examination of the larger particles where the pitted cells are crossed by medullary rays, will enable a careful observer to identify the wood from which the pulp has been made. Thus in Scotch "fir" only one large pit will be seen on

FIG. 52.—Chemical Wood Pulp (Spruce).

FIG. 53.—Chemical Wood Pulp (Poplar).

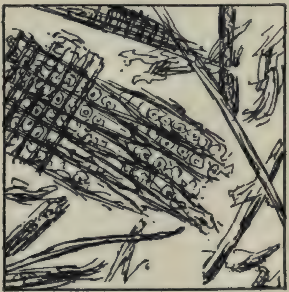


FIG. 54.—Mechanical Wood Pulp.

the cell between two rays, in the fir two small pits, and in the spruce four small pits.

Percentage Composition of Furnish Determined Microscopically.—The sample of paper or other material is reduced to the condition of pulp by boiling with 1 per cent. soda solution, washing and disintegrating by shaking in a bottle with beads. Every care is taken to prepare a representative sample, as already described. The pulp, removed from the wire on which it is strained, must not be mixed with water, which would tend to separate the lighter from the heavier fibres, but three or four portions are removed with the preparation needle and a slide prepared from each. The preparations are stained with the iodine zinc chloride reagent. Take, for example, a piece of news—the mechanical wood fibres will be stained yellow, the chemical blue. A low power is used, and different fields examined in turn, and each time the impression of the proportions in which the fibres are present is recorded. In this way ten fields of view and ten observations are made on each slide and the averages calculated. The mean of each series of observations should agree fairly well with each other, and the mean of the three averages is taken as representing the composition of the furnish. Instead of merely forming an impression by first glance, the numbers of the different fibres in the field of view may be counted.

I give on opposite page a table with a series of figures obtained in this manner. The close agreement of the mean of the three columns A, B, and C should be noted, and is a guarantee of the substantial accuracy of the results, but considerable practice is necessary to obtain uniform figures. The proportion in which the fibres are present cannot be judged straight away from the area covered by the yellow and blue fibres respectively. There is a tendency to over-estimate the proportion of chemical fibres, as these are thin-walled and free from encrusting matters; they are more bulky and weigh less than the encrusted mechanical wood fibres. To correct this impression a number of slides are prepared from papers containing constituents in known proportions for practice. A series of hand-made sheets containing mechanical and chemical wood in known proportions will be found extremely useful in this connection.

TABLE LXXI.

PERCENTAGE OF FIBRES DETERMINED MICROSCOPICALLY (BEADLE AND STEVENS).

	A.		B.		C.	
	Mechanical.	Chemical.	Mechanical.	Chemical.	Mechanical.	Chemical.
1	35	65	50	50	50	50
2	25	75	40	60	55	45
3	30	76	45	55	45	56
4	25	75	50	50	50	50
5	45	55	50	50	40	60
6	75	25	40	60	45	55
7	75	25	60	40	45	55
8	45	50	50	50	50	50
9	50	50	55	45	45	55
10	45	55	35	65	45	55
	455	545	475	525	470	530
Mean	45·5	54·5	47·5	52·5	47·0	53·0

SUMMARY.

	Mechanical.	Chemical.
Column A	45·5	54·5
„ B	47·5	52·5
„ C	47·0	53·0
	140·0	160·0
Mean . . .	46·7	53·3

Mechanical, 46·7 per cent. Chemical, 53·3 per cent.

The method may be applied to determine the percentage composition of any furnish where the fibres take different colours under the action of special reagents. Where this is not the case the problem is more difficult, but can generally be satisfactorily solved provided that a fair proportion of fibres can be easily identified. The method only breaks down in cases where the beating has been prolonged and the majority of the fibres are so distorted as to be no longer recognisable.

Percentage Composition by other Methods.—A rough approximation of the percentage composition may be obtained by treating the sample of paper straight away with reagents. Thus a paper containing mechanical wood or any lignified fibre, such as raw jute, if dipped in a solution of aniline salt (say sulphate), is coloured yellow, and the larger the percentage of mechanical fibre the deeper the yellow. Similarly, a solution of phloroglucinol hydrochloride colours paper containing mechanical wood a rose-red colour ; less than 1 per cent. giving a faint pink, while 60 to 80 per cent. produces a dark red.

These solutions are prepared as follows :—

Aniline sulphate reagent.—1 gram of aniline sulphate is dissolved in 50 c.c. water.

Phloroglucinol hydrochloride (Wiesner).—1 gram. phloroglucinol hydrochloride is dissolved in 50 c.c. rectified spirit and 25 c.c. concentrated hydrochloric acid added.

As certain aniline dyes, such as metanil yellow, are coloured intensely red by hydrochloric acid contained in the phloroglucinol reagent, care must be exercised in drawing conclusions. It is as well to apply the aniline sulphate reagent as a confirmatory test, or to try the action of a few drops of hydrochloric acid alone when no coloration should be produced. Aniline sulphate is also applied in testing for esparto and straw. Papers containing these fibres are coloured pink to red, on warming a sample with the reagent, according to the amount contained in the paper.

Wurster's reagent is a solution of dimethylparaphenylenediamine, termed shortly di-solution. Lignified fibres are coloured red.

Other reagents which may be used for detecting lignified fibres are :—

Naphthylamine hydrochloride, giving an orange-yellow colour.
Anthracene ,, ,, a red colour.
Phenol ,, ,, a blue-green colour.
Pyrrol ,, ,, a purple-red ,,
Ferric ferricyanide solution, ,, a precipitate of Prussian blue in the fibre.
Sulphuric acid 4 parts with water 1 part.
Basic coal-tar dyes and many other substances.

"Amyl sulphuric acid," that is equal parts of sulphuric acid and furfurol free amyl alcohol, warmed in a water-bath to 90° C. until gas begins to be evolved—gives a red-violet to deep indigo-blue colour.

The ferric ferricyanide solution is prepared by mixing a solution of 1·6 grams ferric chloride in 100 c.c. water with 3·3 grams potassium ferricyanide also in 100 c.c. water.

Sulphuric acid (best diluted with a little water) dissolves pure cellulose without darkening, but the merest trace of lignin causes darkening (Klason). For comparative tests 22 grams of the air-dried material (= 20 grams bone-dry) are dissolved in 50 c.c. of the acid in a 100 c.c. stoppered measuring cylinder by vigorous shaking, a test being simultaneously made with a pulp of known degree of lignification. The darker coloured liquid may be diluted until the colour matches that of the lighter for the estimation. The malachite green test (see below) may also be applied to the pulp macroscopically.

Numerous methods have been proposed for the purpose of accurately estimating the percentage composition of the fibrous constituents of a paper by the aid of the foregoing reagents in colour tables, but the results are unsatisfactory. At the best, only a very rough estimate can be made, particularly if the papers be dyed (in which case the dye must first be removed as completely as possible). Also the sizing and loading affects the results and the time that is allowed to elapse between treating the paper and comparing the tints with the standards. Further details are not given here for these reasons. I will only mention that it is better to compare the colours with those produced in a similar manner on papers of known composition than to rely on printed colour-diagrams. The solution must be used in ample excess. The best method is the microscopical one already described.

A relatively small proportion of phloroglucinol (less than 1 per cent.), is sufficient to develop the full colour reaction. If, however, larger proportions are employed, a further absorption of the reagent by the lignone complex ensues, up to 3-6 per cent. by weight, according to the type of lignified fibre operated on. This quantitative relationship is constant and may be employed for the purpose of estimating the amount of a lignified fibre such as mechanical wood in a sample of pulp or paper.

This method (C. F. Cross) rests on a more rational basis than the colour reaction, for the latter appears to be nothing more than a function of a subsidiary grouping in the lignone complex, readily removed by treatment with a small quantity (0·5 per cent. of the weight of the lignified fibre), of hydroxylamin acetate without affecting the main characteristics of the lignone complex. The phloroglucinol absorption is appreciable with unbleached chemical wood, and this must be taken into consideration. Thus a sample of paper gave an absorption number of 3·4, and the mechanical wood from which it was made gave 7·2 and the unbleached sulphite 1·8. This gave 29·6 per cent. of ground wood in the paper. The actual estimation is carried out by treating 2 grams of the sample dried at 100° C. in a dry flask with 40 c.c. of a solution prepared by dissolving 2·5 grams of the pure substance in 250 c.c. water, and making up to 500 c.c. with strong hydrochloric acid. This solution is meanwhile standardised with a formalin solution prepared by diluting 1 c.c. of the ordinary commercial substance with 250 c.c. water and 250 c.c. strong hydrochloric acid. Ten c.c. of the phloroglucinol solution are diluted with 20 c.c. hydrochloric acid (containing equal volumes of strong acid and water), heated to 70° C. on a water-bath, and the formalin solution run in from a burette 1 c.c. at a time with intervals of two minutes between each addition. Towards the end of the reaction the formalin solution is added more slowly, a few drops at a time, and the end point is determined by using a piece of common newspaper as an indicator, taking a drop at a time from the reacting solution and spotting the paper. As long as phloroglucinol is in excess, the mechanical wood in the newspaper gives the usual red colour, and this is rendered sensitive by drying down the spots on the paper by holding the latter some distance above the flame of an ordinary Bunsen burner. A red ring is formed so long as the phloroglucinol is in excess.

The flask containing the paper and phloroglucinol solution is allowed to stand corked over night and 10 c.c. of this is filtered off through a plug of glasswool and titrated in the same manner. The difference between the two figures enables the percentage of mechanical wood to be calculated, after making allowance for the sulphite pulp present. Cross, Bevan, and Sindall give 8·0 as the absorption value of mechanical wood and 1·0 as that of pure unbleached sulphite, and calculate from the following formula :—

$$\frac{100\,(p - 1{\cdot}0)\text{ per cent.}}{8{\cdot}0 - 1{\cdot}0}$$

where p is the phloroglucinol value of the sample of paper.

The standard solutions will not keep and must be made up fresh.

Another chemical method for estimating the proportion of lignin has been suggested by Cross and Bevan, based on the estimation of the hydrochloric acid liberated when a lignified fibre is chlorinated. Any bases previously present must first be removed by treatment with HCl and thorough washing, and then extracted with boiling alcohol to remove the resins. It is then teased out and chlorinated. The chlorine gas must be first washed, by passing through a wash bottle containing water and then through a tower filled with broken glass kept moist. Chlorination should be complete in one hour at 15° C. The excess of chlorine is blown out and the chlorinated product immersed in water and titrated. One c.c. **N** alkali = ·2135 gram mechanical wood (bone-dry).

Sulphite and Soda Cellulose.—According to Klemm, it is possible by means of special reagents to distinguish between sulphite and soda cellulose. The reagent consists of a saturated solution of malachite green—a coal-tar dye —to which 2 per cent. of acetic acid is added. A portion of pulp is treated with a few drops of the reagent, sufficient to soak it, and after allowing it to act for a few minutes the excess of liquid is mopped up with blotting-paper and the fibre washed with water. The fibre is then examined microscopically. Well-bleached chemical pulp remains colourless, partially bleached is coloured sky-blue, and unbleached blue-green to green ; in particular, unbleached sulphite pulp is coloured full green.

Another sample of pulp is similarly treated with a saturated solution of rosaniline sulphate in water containing 2 per cent. of alcohol, to which sulphuric acid is added until the liquid acquires a violet shade. The following colours are produced, according to the origin of the pulp and the extent to which it is bleached :—

Sulphite cellulose—	
Unbleached	deep violet to red.
Bleached	less deep red of less violet hue.
Soda cellulose—	
Unbleached	similar to sulphite cellulose but paler hue.
Bleached	faint reddish hue or colourless.

By testing both with malachite green and rosaniline Klemm is thus able to distinguish between sulphite and soda pulp. There are other methods that are applicable for the same purpose. Thus the proportion of natural resinous matter in sulphite pulp is much higher than in soda pulp, on an average ·5 per cent. in the former as against ·05 per cent. in the latter.

The test depends upon the so-called cholesterine reaction by which resin dissolved in chloroform and treated with acetic anhydride and sulphuric acid yields an intense reddish-purple colour changing to green. It is applied as follows :—

About half a gram of the pulp is treated with 1 to 2 c.c. of chloroform, or better still, carbon tetrachloride, and heated to boiling. In cases where the pulp is strongly compressed it is as well to allow the carbon tetrachloride to stand in contact with the pulp for a quarter to half an hour, occasionally warming the liquid. It is then poured off into a test tube, ½ c.c. of acetic anhydride added, and finally pure concentrated sulphuric acid drop by drop.

In the case of a sulphite pulp a beautiful pink colour first appears, which may be seen very distinctly if the tube be held against a piece of white paper ; this colour quickly disappears, and a further addition of acid produces a green colour. The addition of sulphuric acid should be so made that the liquid separates into two layers, the upper of which is distinctly green, while the under remains colourless. Altogether some six to ten drops of acid are necessary.

In the case of a soda pulp no colour reaction can be detected—at the most, a dirty yellow colour makes its appearance.

PAPER TESTING.

Physical Tests.—The more important physical tests have for their object the determination of the substance, thickness, bulk, strength, stretch, resistance to crumpling and friction, and opacity of papers. In addition, blotting and filter papers are tested for absorbency and permeability, while coloured papers sometimes have to be examined for fastness to light.

C.B.S. Units.—For the present, substance may be reckoned on the metrical system, that is, in terms of grams per sq. meter (for conversion to lb. per ream, see next chapter). A sheet of paper is cut to any convenient size, say 10 cm. square (= 100 sq. cm.), which is conveniently done by means of a metal templet, cutting round the edge with a sharp penknife; or discs may be cut of a uniform size, say with an area of 10 sq. cm., by means of a steel punch 35·69 mm. in diameter. Ten of these discs, or one square sheet, will have a total area of 100 sq. cm. The weight of the paper is accurately determined in grams, and the result multiplied by 100 gives the weight in grams per sq. meter.

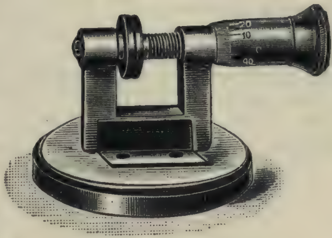


FIG. 55.

Thickness is measured by means of a micrometer screw gauge (fig. 55). The head of the screw should be provided with a friction clutch so that in all tests the same pressure is brought to bear on the sheet, otherwise different figures will be obtained for the thickness according to the pressure exerted by the screw. The end of the screw should be fitted with a small circular plate so as to distribute the pressure over a larger area of paper. In the case of thin papers it is generally better to measure the thickness of several sheets together. A modern form of micrometer gauge registers the thickness in figures on a dial by merely pressing a lever.

Bulk.—This may be defined as the ratio of the total volume occupied by the paper to the volume of fibre it contains. To determine this it is necessary, in the first place, to know the "apparent" specific gravity,[1] that is to

---

[1] By "apparent" specific gravity is meant the specific gravity of the paper as a whole without making allowance for air spaces.

say, $\frac{\text{weight}}{\text{volume of paper}} = \frac{\text{weight}}{\text{area} \times \text{thickness}}$, the figures being expressed in terms of centimeters, sq. centimeters, and grams. The figure for the apparent specific gravity is obtained directly by dividing the thickness of 10 discs (each 10 sq. cm. in area) by their weight in grams.

The percentage by weight of ash or mineral matter in the paper is next determined by burning a gram of paper (see *Determination of Ash*), and from this the weight of mineral in 1 c.c. of paper is calculated by multiplying the percentage mineral by the "apparent" specific gravity of the paper and dividing by 100.

On deducting the figure so obtained from the "apparent" specific gravity (grams of paper per c.c.) there is obtained the actual weight of fibre per c.c. of paper.

There has now been determined per c.c. of paper—

A. Weight of paper.
B. ,, fibre.
C. ,, mineral.

Assuming the actual specific gravity of the fibre contained in the paper to be 1·5, the percentage by volume occupied by the fibre in the paper is obtained by multiplying the weight of fibre per c.c. by 100, and dividing by 1·5. As the specific gravity of mechanical wood fibre is nearer 1 than 1·5 (see table of specific gravity of fibres) it would be better to take a lower figure, say 1·2, when calculating the "bulk" of ordinary news.

Similarly, assuming the specific gravity of the mineral in the paper to be 2·5, the percentage volume occupied by the mineral in the paper is obtained by multiplying the weight of mineral per c.c. by 100, and dividing by 2·5. If now the percentage volume occupied by the fibre be added to that occupied by the mineral, and the sum subtracted from 100, there is obtained the percentage volume occupied by air spaces in the paper.

By dividing the percentage volume of the fibre into 100 (the total volume) a figure is obtained expressing the ratio of the total volume occupied by the paper to the volume of the fibre it contains. This figure represents "bulk" and is a numerical expression for the bulking qualities of the fibres composing the paper.

These considerations are of considerable importance in many classes of paper, among which I may mention blottings. I append a number of figures for bulk obtained for blottings of different make determined in this manner illustrating the calculations described in the preceding paragraphs (see next page).

Distribution of Fibres—Machine and Cross Directions.—Owing to the irregular distribution of fibres the physical properties of papers are not the same in all directions. In machine-made paper the maxima and minima are found in the direction in which the pulp moves with the machine wire on the machine (machine direction) and in a direction at right angles to this (cross direction). Thus the maximum tensile strength and minimum elongation at the moment of rupture are found for strips cut parallel to the machine direction, while minimum tensile strength and maximum elongation are characteristic for strips parallel to the cross direction. This supplies one method of distinguishing the two.

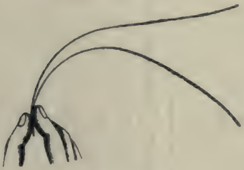


FIG. 56.

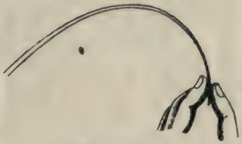


FIG. 57.

A second method is to cut two strips eight or ten inches long, one parallel to the machine or cross direction, and the other at right angles thereto. The two strips are placed together and held at one end between finger and thumb, the other ends standing up in the air and falling over somewhat by their own weight like a couple of plumes. The strip cut in the machine direction is more elastic, and will tend to preserve the vertical position better than the strip cut in the cross direction, and this will be apparent by the latter falling over more if it happens to be underneath (fig. 56). If, however, the strip cut in the machine direction be underneath, the other strip will lie on the top in contact with it (fig. 57). A third method consists in cutting a small disc of the paper and floating it on the surface of water in a basin. The under wet side will expand faster than the upper dry side, and in the cross direction faster than in the machine

TABLE LXXII.

PHYSICAL CONSTANTS OF BLOTTING PAPERS (STEVENS).

Reference No.	$10t$=Thickness of Ten Discs in mm.=volume in c.c.	Weight of Ten Discs in Grams.	Per Cent. Mineral by Weight.	Grams per c.c.			Per Cent. by Volume.			Ratio Total Volume to Fibre Volume or "Bulk."
				Total.	Fibre.	Mineral.	Fibre.	Mineral.	Air.	
1	1·52	·964	15·7	·634	·535	·099	35·6	4·0	60·4	2·81
2	1·68	1·012	9·1	·603	·548	·055	36·5	2·2	61·2	2·74
3	2·12	1·364	·3	·643	·641	·002	42·7	0·1	57·2	2·34
5	2·08	1·290	·5	·620	·617	·003	41·1	0·1	58·8	2·43
6	2·66	1·484	·7	·558	·554	·004	36·9	0·2	62·9	2·71
PHYSICAL CONSTANTS OF DIFFERENT TYPES OF PAPER CHOSEN AT RANDOM.[1]										
Newspaper	·920	·570	8·3	·62	·568	·052	38·0	2·0	60·0	2·6
Art paper	·975	1·13	19·5	1·15	·926	·224	61·3	9·0	29·7	1·6
Periodical	·925	·830	15·2	·897	·761	·136	50·7	5·4	43·9	2·0
Writing	1·22	·51	1·4	·418	·412	·006	27·4	0·2	72·4	2·7
Type-writing	1·65	1·15	12·7	·697	·609	·088	40·6	3·5	55·9	2·4

---

[1] C.B.S. units.

direction, causing the paper to curl up away from the water into the form of a roll. The paper is removed and folded in the direction in which it curls; the crease of the fold then represents the machine direction (fig. 58). If the paper is unsized it must first be sized by soaking in an alcoholic solution of rosin and drying.

Strength and Stretch.—The breaking strain or tension required to rupture a sheet of paper is a physical test to which a large amount of attention has been directed and which is generally regarded as one of the best criteria of quality. For this reason it is in very general use. The more exact machines measure at the same time the breaking stretch or percentage elongation at the moment of rupture, which also affords useful data.

FIG. 58.

For many classes of papers the strength may be taken as an indication of quality. Banks, loans, and the best classes of cotton and linen papers give very high values, as also do the best wrapping papers.

There are numerous machines for testing the strength of paper. They may be divided into two classes.

1. Those which determine the bursting strain. A piece of paper any convenient size is securely clamped round the edges and a force applied to the centre of the sheet. Examples of this type of machine are the Mullen, Southworth and Ashcroft.

In the former a uniform pressure is produced by forcing a liquid (glycerine) against a thin sheet of rubber stretched over a circular orifice, the paper being clamped immediately over the orifice and in contact with the rubber. As the latter expands outwards an increasing strain is exerted on the paper, and the pressure at the moment of rupture is noted on a manometer fitted to the instrument. The disadvantage of the Mullen machine is that it requires to be refilled with glycerine from time to time and the rubber diaphragm replaced by a new one.

Southworth's tester is built on the same principle, the only difference being that the sheet of rubber is replaced by a piston with rounded head which presses against the sheet of paper.

The Ashcroft tester is also fitted with a metal plunger and registers the pounds pressure required to burst or puncture the paper. Careful comparative tests made with this instrument and the Mullen showed a high degree of concordance. The Ashcroft is made in two sizes, one for light papers bursting up to 20 lb. and one for strong papers bursting up to 140 lb. The instruments are small and easily portable.

Bursting strain machines are said to be subject to a considerable personal equation because the results are influenced by the tightness with which the paper is clamped and the rate at which the pressure is applied. The Mullen machine is, however, fitted with a spring clamp which overcomes the first objection, and as to the rate at which the pressure is applied by turning the handle ; this also holds for all hand-operated testing machines, including those testing the breaking strain of a strip. My experience of the bursting strain machines is that they are as accurate and reliable as any other form when kept in proper order. These machines have the advantage that the tests are quickly made, as the paper to be tested has not to be cut to any particular size. Moreover, they test the strength of the paper in all directions in one operation. At one time they were chiefly used in the United States but have now become general in Great Britain. For practical testing of commercial paper they are to be preferred.

2. Machines which determine the tension required to rupture a strip of paper.

The most accurate type consists of a balanced weight lever (as in that of Schopper shown in the illustration).

The tension is produced either by turning a handle, or better, by means of a small hydraulic piston, as shown in the illustration. By this means an even and perfectly regular increase in tension is obtained. The tension is registered on the larger and lower scale, and the stretch on the smaller upper one, and a contrivance is, of course, fitted by which the pointers are arrested at the moment of rupture. To work the hydraulic piston the machine is connected to the ordinary high-pressure water supply, the pressure required being about 44 lb. per square inch.

Every care must be taken in adjusting the strips and fixing them in the clamps. If the strips are not properly adjusted the paper will tear obliquely, or break in the jaws, giving too low a reading.

In no case is it sufficient to test the strength of one strip, but five or ten strips are cut and tested, and the mean of the figures taken as the correct value.

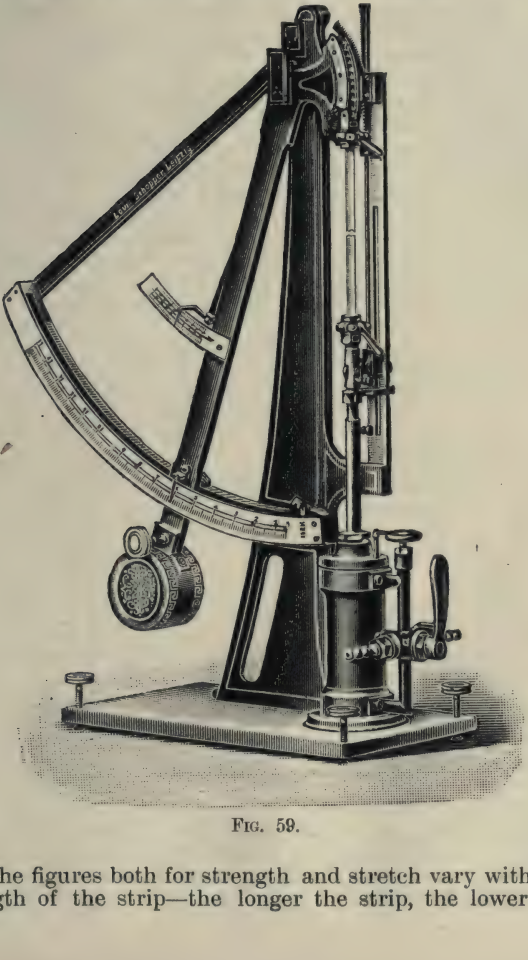


FIG. 59.

The figures both for strength and stretch vary with the length of the strip—the longer the strip, the lower the average value; the differences are not, however, of much importance, but it is as well to make a practice of always using strips of the same length so that all tests are comparable with one another. The breaking strain is also very nearly proportional to the breadth of the strip. On the other hand, the breaking strain and stretch are considerably influenced by the relative humidity of the atmosphere. According to Dalén, the higher the relative humidity the lower the breaking strain and the higher the percentage elongation at fracture. Although strips in machine and cross direction are affected to about the same degree, individual papers differ among themselves as to the extent to which they are influenced. It is sometimes prescribed that the tests shall be made in an atmosphere containing moisture equivalent to 65 per cent. of saturation. For ordinary purposes a table has been compiled giving the correction to be made.

TABLE LXXIII.

FACTORS FOR CORRECTING TENSILE STRENGTH AND ELONGATION FOR RELATIVE HUMIDITY.

Relative Humidity at the time of Testing.	Factor for	
	Breaking Strain.	Elongation.
40	0·88	1·47
45	0·90	1·36
50	0·92	1·25
55	0·94	1·16
60	0·97	1·08
65	1·00	1·00
70	1·04	0·93
75	1·11	0·87
80	1·18	0·80

The influence of temperature has been little studied, but Herzberg states that a higher temperature, if prolonged, reduces both breaking strain and elongation; while, according to Pfuhl, a lower temperature increases the breaking strain, but reduces the elongation.

In testing paper, when strips are cut both in the machine and cross direction, the mean of the average value for each direction gives the mean average value for the paper under examination.

Hygrometers.—To determine the relative humidity of the air the wet- and dry-bulb hygrometer is frequently used. It consists of two similar thermometers on a stand; the bulb of one of these is kept moist by a piece of muslin tied round it, the other end of the muslin dipping into a reservoir containing water. Only in the case where the air is saturated with moisture will both thermometers register the same temperature, the wet bulb usually showing a lower temperature due to the loss of heat caused by evaporation of the water on its surface. The dryer the atmosphere the more rapid is evaporation, and therefore the greater the difference between the temperatures registered by the two thermometers. Taking the temperature of the dry-bulb thermometer and the difference between the readings of the two thermometers, the relative humidity of the air may be ascertained on reference to a table, air saturated with moisture being taken as 100.

As illustrating a series of tests, the following may be given :—

Breaking strains in lb. and stretch per cent., with strips one inch wide and two inches between the jaws.

TABLE LXXIV.

Tensile Strength and Elongation Tests.

Experiment Number.	Strength lb.		Elongation per Cent.	
	M.	C.	M.	C.
1	63·2	60·3	2·8	1·8
2	62·5	54·1	4·2	3·8
3	59·8	54·3	4·2	3·2
4	59·8	57·2	3·8	1·0
Mean	61·33	56·48	3·75	2·45

Hence mean of strength of M. and C. directions = 58·9 lb.
,, stretch ,, ,, = 3·1 per cent.

It will be noticed that the strength is greater in the machine than in the cross direction, while with the stretch the reverse is the case. This is due to the lie of the fibres, a larger proportion of which lie in the machine direction of the paper. Other relations are found in hand-made papers, the preponderating lie of the fibres varying in different parts of the sheet.

Methods of Expressing Tensile Strength.—The breaking strain may be expressed :—

1. In pounds weight for the strips cut to any particular size—say, one inch wide and two inches between the jaws, or, if preferred, in kilograms with strips 2·5 cm. wide and 18 cm. between the jaws.

2. In pounds per sq. inch section or grams per sq. mm. sectional area, as is done with steel and other materials. For this purpose it is necessary to know the sectional area of the strip taken for testing, *i.e.* width × thickness. The width is measured when cutting the strip; the thickness is measured by means of the micrometer, already described. To take an example, a strip 2·5 cm. wide and ·12 mm. thick had a breaking strain of 8530 grams. Its sectional area is $25 \times \cdot 12 = 3$ sq. mm. The breaking strain expressed in grams per square mm. is, therefore, $\frac{8530}{3} = 2843$. The advantage of this form of expression is that it puts paper into a line with other materials: the disadvantage is that it involves the measurement of the thickness which is not susceptible of so high a degree of accuracy as can be obtained with hard resistant materials, such as iron and steel.

3. As "breaking length," that is to say, the length of paper (usually expressed in meters) which would break by its own weight if hung up on end. It is obvious that the figure for breaking length involves the term for "apparent" specific gravity, although it does not involve the measure of thickness. Expressed algebraically: Breaking length (L) = factor (F) × Breaking strain (S). The factor F is the ratio of the length of the strip (l) tested to its weight (g), *i.e.* $F = \frac{l}{g}$ or, by substitution, $L = F\,S = S\frac{l}{g}$. In other words, the breaking length is obtained by multiplying the breaking strain by the length of the strip and dividing by the weight. If the breaking strain be taken in grams, the length of the strip in millimeters, and the weight of the strip in milligrams, the breaking length will be obtained in terms of meters.

It will be seen then that in order to calculate the breaking length we require to know the weight of a strip of known length in addition to the breaking strain. It is not necessary to know either the breadth of the strip or its thickness, and the strip weighed may be of any length, but it is necessary to weigh the strip after using it for determining the breaking strain. Its length is known, as it has been carefully cut to size with a templet. To determine its weight the two halves are dried at 100° C. and weighed in a weighing-bottle.

The breaking length can also be calculated from the breaking strain in grams per sq. mm. by dividing by the (apparent) specific gravity. This gives the breaking length in meters. To illustrate the foregoing I append figures dealing with a thin printing.

Examples: The mean breaking strain for strips one inch (2·5 cm.) wide was found to be 124·8 grams. Each strip was 80 mm. long and weighed ·0528 gram.

Hence breaking length $= 124{\cdot}8 \times \frac{80}{52{\cdot}8} = 189{\cdot}1$ m.

The thickness of ten sheets of the paper was 0·26 mm., and hence sectional area of strip was $25 \times {\cdot}026 = {\cdot}65$ sq. mm. Therefore breaking strain $= \frac{124{\cdot}8}{{\cdot}65} = 192$ grams per sq. mm.

The (apparent) specific gravity was calculated from a series of measurements,[1] and found to be 1·015. Hence breaking length $= \frac{192}{1{\cdot}015} = 189{\cdot}1$ m.

As already stated, the expression "breaking length" involves not only the conception of tensile strength but also that of density or specific gravity. Of any series of papers having the same tensile strength (breaking strain), the higher the density the lower the breaking length. Taking the case of loaded papers, these will have a lower breaking length than unloaded papers of the same breaking strain; that is to say, a considerable difference in breaking length will be shown quite apart from any specific weakening effect produced by loading in a paper.

Breaking length is, therefore, a somewhat complex conception, and figures calculated in accordance with it must be interpreted with caution. If employed as a standard it really means that, if a papermaker increases the density (apparent specific gravity) of his paper, he has got to increase its strength to keep the figure for breaking length up to the same level.

Resistance to Wear and Tear.—Although the figure for breaking strain is of great value in judging the quality of a paper, this test does not reproduce the whole of the conditions to which a paper is subjected. For this

---

[1] See C.B.S. units.

purpose a rough test has long been in use. A sheet of paper not larger than quarto size is crumpled up in the hand into a ball and then spread out again on a flat surface; the process is repeated until small holes can be seen on holding the sheet up to the light. The more resistant the paper, the more often the process of crumpling and unfolding can be repeated before holes are detected. With very resistant papers the sheet is rubbed between the hands in the same manner as when washing a cloth. To replace this rough and ready test the following mechanical testing apparatus have been devised:—

1. *Kirschner's Creasing Roll* (fig. 60).—This consists of a roll, 16 cm. in diameter and weighing about 6 kg. The outer edge of the roll is provided with a flange, which fits a groove in a metal rail along which it can be rolled. A strip of paper, such as is used for testing the breaking strain, is lightly folded with the hand and laid in the groove, and then creased by running the roller over it; the strip is then turned over and creased in the opposite direction. The breaking strain of the strip so treated is tested in the ordinary manner, and as the paper is now weaker at the spot where it has been creased it will give a lower figure than before creasing. In a similar manner the stretch will also be lower. The difference between the figures obtained before and after treatment is termed the creasing or folding loss and is a measure of the resistance of the sample of paper to folding and crumpling. Numerous tests have shown that the creasing or folding loss is greater in the case of the stretch than of the breaking strain. Further, as regards the stretch the folding loss is generally greater in the machine than in the cross direction, whilst as regards the breaking strain the reverse is the case.

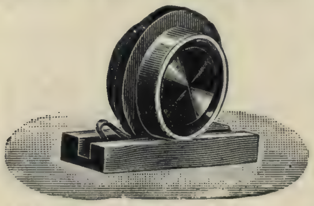


Fig. 60.

There is no close agreement between the figures obtained with Kirschner's roll and Schopper's folding machine described below, but the folding loss generally decreases with increased resistance to friction, as measured with the latter machine.

2. *Pfuhl's Friction Machine.*—The sheet of paper is drawn between sheets of rubber kept close together by air pressure. The air pressure necessary to produce sufficient friction to rupture the paper is termed breaking pressure, and forms a measure of the resistance of the paper to friction. The weak point in this machine is the wear on the rubber and consequent alteration in nature of the surfaces in contact with the paper which leads to varying results.

3. *Schopper's Folding Machine.*—This machine has been generally adopted in Germany as the best adapted for measuring the resistance of paper to folding and friction. It is of somewhat elaborate construction and unfortunately costly. A strip of paper 15 mm. wide is placed between clips attached to springs which keep it taut under a tension of 1 kg., while it is folded in the middle—first one way, then the other, by a metal plate which advances and recedes, worked by a motor. The number of double folds thus effected on the strip is recorded automatically until the strip breaks, which throws the mechanism out of gear. The number of double folds a paper will stand before breaking is a measure of its resistance to folding and friction.

The following tables have been constructed for Pfuhl's and Schopper's machines. The percentage saturation of the atmosphere is taken at 65 per cent. :—

TABLE LXXV.

COMPARATIVE FIGURES FOR FOLDING AND FRICTION MACHINES.

Stages for Resistance to Friction.	Pfuhl's Machine. Breaking Pressure in cm. of a Column of Mercury.	Schopper's Machine. Number of Double Folds.
0. Extremely low	—	0·2
1. Very low	0·3	3·6
2. Low	3·6	7·19
3. Medium	6·16	20·39
4. Fairly high	16·26	40·79
5. High	26·48	80·189
6. Very high	At 50 must stand 2·3 treatments.	190·999
7. Extremely high	At 50 must stand more than 3 treatments.	1000 and over.

Opacity of Papers.—Where comparative tests only are required it is merely necessary to determine the number of sheets which, laid on the top of one another, will obscure an object on which they are placed. A convenient method is the following (Winkler): A cross, letter, or other mark in black, is painted on a sheet of thin glass; sheets of paper are laid on this and covered with a second sheet of glass to keep them in position. The whole is then held up to the light at arm's-length to see whether the mark is visible through the sheets. By repeated trials the number of sheets is determined which just suffices to render the mark invisible. The operation is then repeated with a standard paper. The opacity of individual sheets will then be inversely as the number required to render the mark invisible. In many cases a more practically useful result will be obtained by taking the thickness of the papers into account by measuring in each case the thickness of the layer of sheets required in the tests. The opacity of the paper material irrespective of the thickness of the sheets (specific opacity) will then be inversely as the thickness of the layer of sheets required.

To determine the absolute opacity a source of light of standard brilliancy is required. Klemm's diaphanometer is provided with a standard one-candle power lamp at one end of a tube, in the middle of which is a clamp to take sheets of paper, and the light is viewed through the paper by an eye-piece at the other end. The principle involved is that already described, a sufficient number of sheets being inserted in the clamp to render the source of light invisible.

In order to obviate the necessity of a standard light and the exclusion of other light from the instrument, Beadle devised a portable opacity meter which has proved itself of very great service for the registration of the relative opacities of paper. This instrument consists of a brass tube 10 inches long by 1½ inches in diameter; the end which is raised to the eye is plain, the other end which is made to hold the paper has fitted over it a brass collar with a disc, in the centre of which is a hole ⅜ of an inch in diameter. The brass collar, which is detachable, is made to hold discs of standard opacities; these can be made either of frosted glass, but preferably of different thicknesses of paper, enclosed between glass discs and fastened together by a brass ring. A disc puncher, somewhat similar to a cork borer, is required for punching the discs of paper under observation. To arrive at the necessary illumination, a disc of the standard opacity is placed in the instrument, which is held to the eye in a horizontal position. If in daylight, the observer moves his head sideways until he reaches a spot in the room at which the light is just extinguished, the left eye of course being kept closed. Having noted this position in the room, he immediately removes the standard opacity disc and inserts such a number of discs of the paper under observation as to just obscure the light. The transparency of the paper in question may be expressed as the number of sheets necessary to extinguish the light or as the specific transparency of the substance of which the paper is composed (which is a figure independent of the thickness of the sheet), and is obtained by measuring with a micrometer the total thicknesses of the discs necessary to just extinguish the light. If the sheets are very thick or very opaque it is advisable to use No. 2 opacity screen, which has double the opacity of No. 1 screen, the observed figures in this case being divided by 2.

When the observation is made by gas or electric light the observer, with the instrument to the eye, approaches the source of light until the light is just visible through the screen, he then moves it slightly upwards until the light is just extinguished.

Sizing Qualities of Papers.—A rough idea may be got by making heavy ink marks in the form of a double cross (♯) on the paper with a quill pen which does not scratch. When dry, the reverse side of the sheet is examined to see if any ink has penetrated. The sheet is also torn through the spot where the ink lies to see how far it has penetrated into the fibres or the sheet may be cut at this spot and examined edgeways under the microscope. The ink used should be of some standard quality, and from a freshly opened bottle, if possible, and not from an ink-pot where it has been exposed for some time to the air.

Herzberg suggests the use of a mechanical drawing pen in testing insufficiently sized paper, the thickness of the strokes made being increased until the ink strikes through to the under side; the width of the stroke is then a measure of the sizing qualities. The pen should always be held at the same angle, and the stroke should be made by drawing the pen over the surface of the paper at the same rate.

Numerous methods have been devised for expressing the sizing qualities numerically by treating the two sides of the sheet with different liquids which develop a coloration when they meet in the paper. The use of alcoholic or ethereal solutions for this purpose, except for tub-sized papers, is obviously not permissible, as they possess a powerful solvent action on the rosin of the size quite distinct from that of a watery fluid like ink. The best method is that worked out by Schluttig and Naumann[1] who use an aqueous solution of ferric chloride (100 c.c. water, 2·9 grams ferric chloride, containing 1 gram iron, 1 gram gum arabic and ·2 gram phenol) and also a solution of tannin (1 per cent. solution, containing 2 per cent. phenol). These solutions, if mixed, form a black insoluble substance similar in composition to ink which has dried on paper. The sheet of paper to be examined is supported on a frame at an angle of 60° to the horizontal (fig. 61). By means of a triple pipette three vertical lines are formed on the sheet of paper by allowing the ferric chloride solution to trickle down the surface. After standing for a quarter of an hour, the sheet of

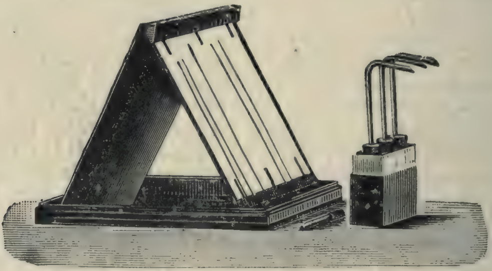


FIG. 61.

---

[1] Herzberg states that in some cases the results obtained by this test do not correspond with tests made by drawing ink marks on the paper. It is, however, retained for the present as there is not sufficient data to enable a decision to be reached in the matter, and no other satisfactory test has been proposed. Further research is very desirable and should include a comparison of papers with different inks.

paper is turned over and at the same time turned halfway round, so that the faint marks already produced are now on the under surface of the sheet, and lie horizontally instead of vertically. Three similar marks are now made on the upper surface by allowing the tannin solution to trickle down in the same manner as before. The three marks on one surface will now cross the three marks on the other surface at nine points. When the tannin solution on the upper surface has penetrated to the place where it meets the ferric chloride solution, a dark stain will be produced by a chemical reaction between the two at one or more of the nine points. If black marks appear at all nine points within a few seconds the paper is soft-sized. If grey or black marks begin gradually to appear after a lapse of some minutes the paper may be considered hard-sized, while no marks appear for twenty-four hours or more with very hard-sized papers. The method is open to the objection that the liquids used for testing the degree of penetration are in neither case ink. The methods first described use ink and therefore reproduce better the conditions under which paper is actually used, and should therefore be given preference. They can also be modified by using different varieties of ink. I may mention here that commercial inks differ considerably in composition, especially as regards the percentage of free acid. A formula for a standard ink on a scientific basis has been worked out by Schluttig and Naumann, and has been adopted for official purposes, and for records by the State of Massachusetts, U.S.A. The composition is as follows: Dry gallotannic acid, 23·4 parts; gallic acid crystals, 7·7 parts; ferrous sulphate, 30 parts; gum arabic, 25 parts; dilute hydrochloric acid, 25 parts; and phenol, 1 part in 1000 parts of water.

Some inks on the market, including some of those used for stylographic pens, are not iron tannin inks, but merely solutions in water of coal-tar dyes and other colouring matters. They should not be used for the above tests, as they have less tendency to penetrate the paper, giving misleading results.

Absorbency of Blotting Papers.—The absorbency is measured by the rate at which water rises in a vertically suspended strip of paper with the lower end dipping in the liquid. This is commonly called the mounting test.

Either the time is noted which the liquid takes to rise to a given height, or the height to which the liquid rises in a given time. The latter is the more usual method and the time allowed is generally five minutes. It is customary to use water, although it is obviously preferable in some cases at any rate to use ink. The two liquids may give very different figures, that for ink being much lower for papers giving low results in the zone test to be subsequently described. When the end of the strip is immersed the liquid rises rapidly at first, but the rate of rise gradually falls off and there is a difference between the rate of rise in the machine and cross directions, the rise being more rapid in the former than the latter; I have also found, as might be expected, that the temperature influences the rate of rise which increases with rise of temperature.

The strip for the test is taken one inch wide, the last half-inch from the bottom being marked off with a ruled pencil line, and the suspended strip immersed in the liquid up to the pencil mark.

The apparatus employed is usually of a simple nature, consisting of a clamp to hold the strip of paper, which can be lowered and fixed in position by a thumbscrew. In working such an arrangement a good deal of difficulty is experienced in immersing the strip rapidly and at the right moment into the water exactly up to the pencil mark. It is necessary that the strip be immersed rapidly, as otherwise water begins to rise in the paper beyond the pencil mark before this mark is on a level with the water in the containing vessel. In attempting to lower the paper rapidly it is either not immersed far enough or else gets immersed too far, the result being that, in spite of every care taken, the results of a number of tests on the same paper differ considerably among themselves. These differences frequently amount to 5 per cent. or even 10 per cent. of the total rise measured. To allow of accurate determinations of the measurement of the rate of rise of water or other liquid in a strip of blotting paper, I have devised a blotting tester or bibliometer (fig. 62). It permits of rapidly immersing the strip exactly to the required depth in the water. The strip is affixed at its upper end by a metal spring to a movable arm, which can be raised or lowered by means of a cam. In the illustration it is shown in the raised position. Its position when lowered is regulated by means of a stop screw. The head of the stop screw is on the left of the support, near the top. The arm consists of a metal plate, in front of which

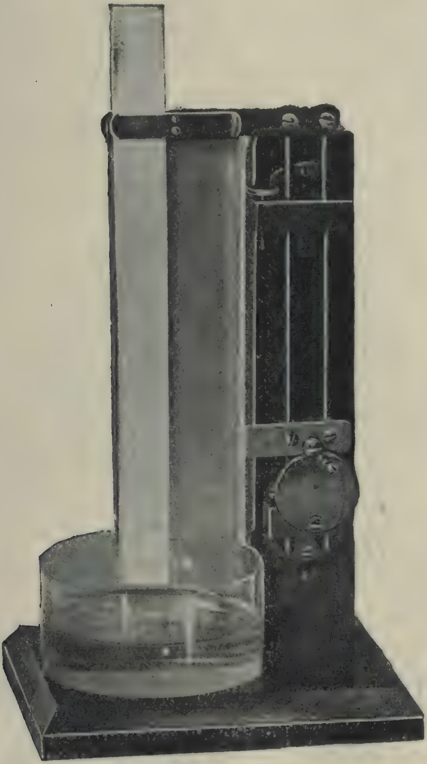


FIG. 62.

hangs the paper strip at a distance of about a quarter of an inch from the face of the metal. The strip is held in place by a spring clip, which allows of easy adjustment. The bottom of the metal plate is provided with two small projecting pieces, and the stop screw is so adjusted that, on lowering the slide, these projecting pieces just touch the surface of the water. The slide is now raised so as to be in the position shown in the illustration, and the strip of paper, having a line ruled across it at a short distance from the lower end, is now fixed by the metal spring and adjusted so that the pencil line is exactly level with the points of the projecting pieces at the bottom of the plate. When now the slide is lowered by means of the cam, the strip of paper will be rapidly immersed in the water up to the pencil line. The water should rise evenly in the strip, and a slight pencil mark can be made at the spot to which it has risen after a given number of minutes (say, five). This is best done with a point of a pencil, pressing the strip well back on the metal plate, or more roughly by a scale fixed alongside of the strip of paper. The instrument is provided with the arm sufficiently large to take two strips at a time, so that two papers can be compared if required. On the other hand, it is not possible to test more than one at a time, if accurate measurements are desired. The error need never exceed one millimeter, and if the mean is taken of three or four tests, the error will not probably exceed a fraction of this. Tests are made both in the machine and cross direction and the mean of both averages taken. For ordinary purposes one test will give a sufficiently accurate result. The water in the reservoir should be kept at a temperature of 15° C. (60° F), if accurately comparable results are to be obtained, as the temperature has a very marked effect on the rate at which water rises in a strip of blotting paper.

Loss of Absorbent Qualities and Zone Tests.—Although the "mounting" test just described is a useful indication of the rapidity with which liquids are absorbed, there are other and perhaps more important qualities affecting the absorbency which it does not take into account.

In the first place, the "bulk," which is a measure of the volume occupied by air spaces in the paper, should be considered. As a general rule the greater the bulking qualities the better; this is also brought out by the fact that papers with good bulking qualities give high figures with mounting test. Something more can be learned by substituting ink for water in the mounting test. If a much lower figure is obtained it points to deficiencies brought out by the "zone" test. Blotting paper should not lose its absorbent qualities on repeated use. This is an important point which is frequently lost sight of. In the ordinary way the ink marks left on a a sheet of blotting dry in, and when the sheet is used again the writing will be smudged if the paper at these marks is no longer absorbent. To test this point a large ink-blot is made by allowing 1 c.c. of fresh ink (the same make of ink should always be used for comparative tests) to flow on to the surface of a sheet of the paper to be tested, which is conveniently supported in a horizontal position by placing it on the top of an ordinary tumbler or beaker. The ink is allowed to dry in, and that part of the paper covered by the blot tested for its bibulous qualities by drawing a pen full of ink right across the blot (fig. 63). Where the paper is absorbent the ink spreads and where non-absorbent it behaves like a sheet of sized paper. With blottings which lose their absorbent qualities on repeated use, two points are to be noticed : (1) the formation of a non-absorbent ring or zone at the outer edge of the blot ; (2) the more or less pronounced loss of absorbency in the interior portion of the

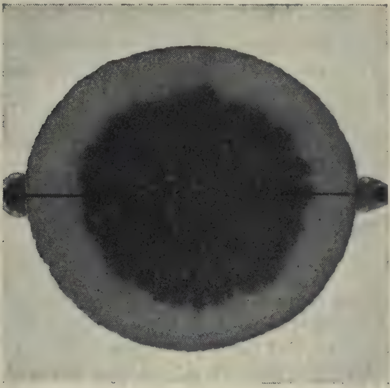


FIG. 63.

blot. The areas occupied respectively by the zone and inner portions of the blot may be calculated by measuring the total diameter of the blot and inner portions in two directions at right angles to one another; on subtracting the mean diameter of inner portion from the mean total diameter the proportion of non-absorbent diameter is obtained. As an example of the variations met with, I quote the following:—

TABLE LXXVI.

Zone Tests with Blotting Papers.

Sample.	Outside Diameter of Blot.	Proportion of Non-absorbent Diameter.	Percentage of Zone on Total Diameter.
1	85 mm.	11 mm.	13·0
2	80 ,,	8 ,,	10·0
3	80 ,,	4 ,,	5·0
4	85 ,,	1·5 ,,	1·7

Of course, these figures are only approximate, as the zone is not of uniform width all the way round nor is the blot perfectly circular, but the figures are sufficiently accurate for comparative purposes. As to the percentage area of the whole blot actually occupied by the non-absorbent zone, this is readily calculated, if desired, thus: taking sample (2) above, the areas are as $40^2 : (40 - 4)^2$ or as 1600 : 1296; that is, area of non-absorbent zone is 19 per cent. of total area of blot.

Herzberg published comparative "mounting" and zone tests on 14 samples of blotting paper and concluded that generally the higher the figure for the mounting test the larger the non-absorbent zone, so that samples arranged in order of quality by the mounting test would be reversed if the zone test were adopted. This opinion is based on the following figures which he obtained, given on the next page.

The far-reaching conclusion that the mounting height and non-absorbent zone are in inverse order cannot be admitted. With the exception of samples 1 and 4, all

TABLE LXXVII.

ZONE AND MOUNTING TESTS (HERZBERG).

No. of Sample.	Weight in Grms., Per Sq. Mm.	Description.	Ash Per Cent.	Mount in 10 Minutes, Mm.	Per Cent. Non-Absorbent Zone Iron Gall Ink.
1	141	Deciduous wood pulp with the addition of cotton . .	3·0	202	20
2	175	Deciduous wood pulp with a small quantity of cotton .	1·3	195	14
3	178	Deciduous wood pulp	1·0	189	13
4	119	Cotton with a small quantity of linen .	1·0	132	7
5	113	Cotton with a small quantity of linen .	0·8	121	10
6	142	Cotton and deciduous wood pulp . .	3·0	90	13
7	137	Coniferous wood pulp	0·8	89	11
8	58	Cotton and linen .	0·8	85	10
9	78	Cotton . . .	2·8	68	10
10	67	Cotton and linen .	0·8	59	12
11	143	Deciduous with a little coniferous wood pulp . .	0·5	52	13
12	64	Cotton and linen .	3·0	44	10
13	86	Cotton with a small quantity of linen .	12·8	34	10
14	157	Cotton with a small quantity of linen .	1·0	31	13

give very similar figures for percentage of non-absorbent zone which lie between 10 and 14. Sample 1 certainly gives the highest figure in the mounting test and the largest non-absorbent zone, but sample 4, which gives a very good mounting test, has the smallest non-absorbent zone.

Beadle and Stevens found that lime salts were generally the cause of the non-absorbent zone and that the removal of these led to a less pronounced zone or even a zoneless paper. Herzberg questions this statement but brings forward no evidence. He suggests, however, that the zone is mostly conditioned by the solid constituents of the ink. This view can easily be shown to be incorrect, for an ink giving a wide zone with some blottings will be found to give no zone at all with the very best filter papers.

Loss of absorbency may be tested in another way. Pieces of blotting cut to a size sufficiently large to take a good-sized blot—say, three or four inches square—are laid on the surface of ink in a shallow dish. When soaked they are removed, allowed to drain and dry in the air. These sheets represent blotting paper, the whole surface of which has been once used and the absorbency may be tested by the mounting test, or as follows :—

Drops of ink are allowed to fall on the surface of the paper from a burette, and the time is noted which is required for the drops to be absorbed ; that is to say, for the wetness of the surface to disappear. This will be appreciable in most, if not all cases. The drops from an ordinary burette usually equal about ·05 c.c., and the best paper will only require half to one second to absorb the blot, other papers will take two or three seconds, and inferior papers as much as five seconds. This test can also be carried out on the untreated paper. Instead of allowing the ink to fall drop by drop Reed prefers to allow 1 c.c. of ink to run from a pipette and notes the time taken for the wetness to disappear. Conclusions may also be drawn from the shape of the splash and blot formed by a drop falling from a height (8 in.) on to the surface of the paper. Better papers give blots whose final shape is more regular and freer from radiating lines than inferior papers.

Other properties of blottings, besides absorbency, must not be lost sight of. Thus the paper must be sufficiently compact and strong to stand rubbing with the hand without loosening the surface and should possess a small bursting strain.

Examination of Filter Papers.—Papers of this class are examined for penetrability by fluids and power to withhold finely divided substances, including chemical precipitates. To a certain extent these two qualities are incompatible. In order to effectively retain finely-divided substances the pores in the paper must be very small, consequently the paper is less rapidly penetrated by liquids.

Nevertheless papers are made which combine both advantages to a large extent.

Penetrability is measured by determining the time taken by a given quantity of fluid, say 100 c.c., under a constant pressure, say 5 cm., of water, to pass through a sheet of filter paper (a disc 5 cm. diameter). An apparatus (fig. 64) has been designed by Herzberg, and consists of a

FIG. 64.

cylindrical reservoir of water with an air-tight cover and tube-funnel passing through it. This admits of adjusting the pressure of water on Marriott's principle. Connected with this, by a tube provided with a cock, is a cylindrical box, 5 cm. diameter, to take the filter paper. The upper half of this box is unscrewed and the cock turned on slowly, so that the water rises in the box until it reaches the edge ; the sheet of filter paper is now laid in position and the top half of the box replaced. The cock is now turned on again until water issues in a regular stream. The time taken to collect 100 c.c. in a measuring flask is then noted, from which the amount passed per minute is calculated. This will usually lie between 20 and 800 c.c., working with a pressure produced by 5 cm. of water.

The power to retain finely-divided substances may be tested by filtering fine precipitates of barium sulphate or calcium oxalate through the sample of filter paper in the ordinary manner. The size of the particles of a precipitate will depend on the concentration of the solutions and other details of its preparation. Herzberg recommends the following solutions: Barium chloride, 122 grams per liter, and potassium sulphate 87 grams per liter. Equal volumes of the solutions are mixed, and one lot filtered hot, the other cold. The best papers retain the whole of the precipitate, even from the cold mixture (heat tends to increase the size of the particles), and yield clear filtrates. For most chemical purposes it is sufficient if the precipitate from the hot liquid is retained completely.

Some special filter papers on the market have great retaining power for fine precipitates, but have such low penetrability (filter so slowly) that they are of little value for ordinary purposes.

Chemical Analysis of Paper.

Mineral Constituents.—Having shown how it is possible to identify the fibrous constituents of paper and estimate the proportions in which they are present, I now proceed to the analysis of mineral constituents. The methods employed are chemical, rather than microscopical. This section falls into two parts ; firstly, the determination of the percentage of loading, secondly, the composition of the loading.

1. *Percentage of Loading.*—This is determined by burning the paper to an ash, which is weighed, and its weight calculated as a percentage on the original weight of the paper. All papers when burnt leave a residue of ash, even those in which no loading materials have been added in the course of manufacture, as paper-making fibres without exception contain traces of mineral matter which are not removed in boiling and bleaching. This mineral matter is so intimately associated with the fibre that it is not removed by the ordinary chemical treatment (see table, p. 223, Ash of Fibres). The mineral matter dissolved in water, the lime in the bleach liquors, and mineral matter, such as alum with the size, all contribute something to the mineral matter in the paper, so that the percentage of ash from these sources may amount to 2 per cent. A higher figure than this will probably point to the addition of loading. Under the term mineral matter must be included mineral earth colours which act like loading and are left as a residue on burning the paper. In the air-dry condition all mineral matter retains a small proportion of moisture, and gypsum, in addition to natural moisture, contains water chemically combined, as it is a combination of calcium sulphate with two molecules of water as $CaSO_4 . 2H_2O$. In the process of burning paper to ash, this water is of course driven off, so that the proportion of air-dry loading in the paper will be somewhat in excess of the percentage of ash; on the other hand, this error is somewhat compensated for by the mineral matter naturally present in the fibre, which, in the form of ash, is ordinarily reckoned as loading.

It is convenient to weigh off 1 gram of paper for analysis, which is then ignited, preferably in a platinum crucible; the crucible itself may be weighed either before the analysis or after burning the paper to ash, and wiping out with a dry cloth. The paper should be burnt to a white ash, free from black or charred portions. It is a good plan after weighing to ignite a second time and weigh again. If the second weighing should show a loss in weight, the ignition is repeated until the weight is constant. Of course paper containing iron, such, for instance, as that loaded with oxide of iron colours in the form of ochres, golden oxide or iron compounds, such as Prussian blue, will give an ash of a yellow or reddish shade. The colour of the ash may thus afford a clue to the constituents of the paper.

Ultramarine and smalts are not affected by heating, and therefore impart to the ash a bluish shade, but the amount added for toning white papers is generally insufficient to impart an appreciable colour. Lead chromate (chrome yellow) may also survive the ignition, imparting a yellow colour to the ash. The ash of the paper usually retains the form of the sheet, and is very light and friable where the paper contains little or no loading. The crucible with contents must, therefore, be shielded from any draught lest pieces be blown away and lost.

2. *Analysis of Loading.*—A complete chemical analysis of mineral matter is an operation requiring considerable skill and experience. It is hardly to be attempted by any but those who have specialised in chemical analysis, and no attempt will be made here to treat the subject fully; for detailed instructions the reader is referred to some textbook on mineral analysis. Some idea of the constituents can be obtained by judicious application of the following tests. A good quantity of the paper is burnt so as to yield, if possible, ½ to 1 gram of ash to work on. It is transferred to a test tube and gently warmed with a small quantity of dilute hydrochloric acid. If the whole of the ash goes into solution, it is a proof that aluminium and magnesium silicates, and barium sulphate, in any of their various forms are absent. One or two treatments with fresh quantities of acid may be necessary to dissolve the whole of the soluble ash, pouring off each time through a filter paper. We now have :—

(1) A solution.
(2) An insoluble residue.

1. *Examination of the Solution.*—A yellow liquid points to the presence of iron. A portion of the solution is made alkaline with ammonia, and heated, when the iron is precipitated in reddish-brown flocks. If no iron is present there may still be a white gelatinous precipitate consisting of alumina derived from a partial decomposition of clay (aluminium silicate) or residues of alum dissolved by the hydrochloric acid. The precipitate is filtered off, and a few drops of ammonia added, unless the liquid still smells strongly of that reagent. To the clear solution is added a small quantity of a solution of

ammonium oxalate and the liquid heated. A white precipitate points to the presence of calcium; this calcium existed in the paper previous to ashing, either as carbonate or sulphate; in either case it was dissolved out of the ash with hydrochloric acid. To ascertain whether it is derived from calcium sulphate, a fresh portion of the filtered hydrochloric acid solution is tested for sulphate by adding a few drops of barium chloride solution, and warming. The presence of sulphate causes the formation of a white precipitate of barium sulphate.

2. *Examination of Insoluble Residue.*—The residue insoluble in hydrochloric acid, if any, is dried in the oven and intimately mixed with four or five times its weight of fusion mixture.[1] The whole is placed in a platinum crucible and gradually heated over a Bunsen burner and finally for ¼-hour in a blow-pipe flame; the whole contents of the crucible should reach a state of quiet fusion. When cold the mass is extracted with water by placing the crucible bodily in a beaker, covering with distilled water and heating gently for some hours. When the contents are loosened and disintegrated the crucible is removed and the alkaline solution filtered off, finally transferring the insoluble residue to the filter paper and washing thoroughly with hot water. The fusion process has caused the silica of the china clay and other silicates to combine with sodium, forming sodium silicate soluble in water; similarly the sulphuric acid derived from barium sulphate combines with sodium to form soluble sodium sulphate; these will, therefore, be contained in the filtrate. On the other hand, the aluminium of the clay, the magnesium of the magnesium silicates, and barium of the barium sulphate remain insoluble as hydroxides and carbonates, and will therefore be found in the residue on the filter paper.

1. *Examination of the Soluble Portion.*—This is made acid with hydrochloric acid and evaporated to dryness. It is then taken up with some fresh hydrochloric acid and hot water, when the silica will be obtained as transparent flakes and filtered off. The precipitate of silica may be easily missed, as it is gelatinous and transparent. The presence of silica points to silicates in the original ash. The solution from the silica is treated with a few drops

---

[1] Fusion mixture consists of dry sodium and potassium carbonates mixed in equal proportions.

of barium chloride solution, and heated. The formation of a precipitate points to the presence of sulphuric acid derived from barium sulphate in the original ash.

2. *Examination of Insoluble Residue.*—The residue is dissolved in dilute hydrochloric acid and the solution precipitated with ammonia. A white flocculent precipitate points to aluminium derived from aluminium silicate (clay) in the original ash. The precipitate of alumina is filtered off, and ammonium carbonate solution added to the filtrate. A white precipitate indicates barium. The filtrate from the precipitates formed with ammonium carbonate is treated with a few drops of sodium phosphate solution and shaken vigorously. A white precipitate indicates magnesium derived from magnesium silicate in the original ash.

To sum up: the presence of silica and alumina point to aluminium silicate in the form of china clay, etc. Silica and magnesium point to magnesium silicate in the form of asbestine, agalite, talc, etc. Sulphuric acid and barium point to barium sulphate as *blanc fixe*, etc. With ½ gram or more of ash for analysis, the precipitates should be fairly heavy and no notice need be taken of slight cloudiness or opalescence. Traces of alumina will generally be found derived from the alum used in sizing whether china clay has been added or not, also traces of lime derived from the water, bleach liquors and other sources.

Iron in paper is best determined colorimetrically. The ash from a given weight of paper is dissolved by digesting with hydrochloric acid and a drop or two of nitric acid. The solution is then transferred to a Nessler tube and diluted with water. The percentage of iron is estimated by the use of ferrocyanide solution and matching the blue tint with a standard iron solution, as described in the estimation of iron in water, alum, etc. The subjoined table gives the percentage of iron in a number of papers:—

TABLE LXXVIII.

IRON IN VARIOUS PAPERS (BEADLE).

	Pts. of Iron per 100,000.
Iron in News—	
8 Different samples analysed.	
Greatest amount	60·0
Least amount	4·0
Mean	39·6
Periodicals and Journals—	
13 Different samples analysed.	
Greatest amount	30·0
Least amount	3·0
Mean	16·7
Book Papers—	
4 Different samples analysed.	
Greatest amount	25·0
Least amount	8·0
Mean	12·5
Mean of all analyses of all papers tested	22·9

In examining coated papers the mineral in the coating is first removed by soaking the paper in water and going over the surface with a camel's hair brush. The mineral matter detached in this manner from the body paper is collected on a filter paper, washed with water and examined separately from the ash of the body paper. The microscope can often render service in the examination of mineral matter. I give drawings of different loading materials, as seen under the microscope (figs. 21-32). Unfortunately, the ignition of the paper often destroys the characteristic appearance of the mineral matter; on the other hand, the characteristic forms may sometimes be regenerated. Thus, if a little of a paper containing gypsum be warmed with a few drops of water which is then concentrated to a very small bulk and a drop placed on a microscope slide and allowed to cool, any gypsum dissolved from the paper separates out again on cooling in characteristically shaped crystals.

Moisture in Paper.—The percentage of moisture in paper varies with the relative humidity of the atmosphere to which the paper is exposed. The accompanying table gives the percentage of moisture in sheets of paper which have been freely exposed to an atmosphere of varying humidity:—

TABLE LXXIX.

MOISTURE CONTAINED IN PAPER EXPOSED TO AN ATMOSPHERE OF VARYING HUMIDITY (HERZBERG).

Relative Humidity or percentage Saturation of the Air.	Moisture in Paper.
100	21·5 per Cent.
90	13·5 ,,
80	8·9 ,,
70	8·4 ,,
60	6·5 ,,
50	5·6 ,,
40	3·4 ,,
30	2·3 ,,

It seldom happens that paper is freely exposed to the atmosphere. As it comes from the drying cylinders, and is reeled or cut and stacked, it is dryer than it would be if freely exposed to an atmosphere of average humidity, hence when packed and stored it usually takes up moisture with increase of weight. The moisture will not be taken up evenly, so that the edges and top sheets will be wetter than the centre, unless the paper has been stored for a considerable time and the moisture penetrated right through. The conditions are therefore similar to those dealt with in the estimation of moisture in pulp. Circumstances are not such as to require the sampling of paper, so that this aspect of the question need not be further discussed. In the laboratory, however, it is at times necessary to determine the percentage of moisture in paper or to weigh the sample under examination when it is "bone-dry" for calculating the percentages of other constituents on the "bone-dry" weight. The paper is cut to a convenient size, usually in the form of a strip, one to two inches wide, which will roll up and fit into a weighing-bottle. The weight of the moist or air-dry strip and bottle are first determined and the strip dried in an oven at 100° for half an hour. It is then quickly made into a roll, inserted in the weighing-bottle, which is left in the oven with the stopper out for a little while longer, after which the stopper is replaced and the bottle allowed to cool and reweighed. The weight of "bone-dry" paper is obtained after subtracting the weight of the bottle, and the difference between this and the original weight of the paper gives the weight of moisture it contained.

NATURE AND PROPORTION OF SIZE.

Vegetable Size.—The detection of vegetable size resolves itself into an examination of paper for the presence of rosin. Although insoluble in water, rosin dissolves readily in alcohol; a small piece of the paper is therefore extracted by warming in a test tube with sufficient rectified spirits (not methylated spirits) to cover the paper. The paper may be torn up into small pieces or folded in a sort of accordion pleat, in order to take up as little space as possible and permit of the extraction with a small quantity of alcohol. When cold the liquid is poured off into a test tube half-full of water. The alcoholic liquid floats on the surface of the water and at the point of junction the resin is precipitated as a whitish ring. On placing the thumb over the mouth of the test tube and inverting once or twice, the liquids are mixed and take an opalescent appearance in the presence of rosin. Rosin may also be tested for, as described in the examination of sulphite pulp for resins. Another test consists in allowing a drop of ether to fall on the surface of the paper; the ether dissolves the rosin, which, on evaporation of the ether, separates out again in the form of a ring.

To estimate the amount of rosin present, one to five grams of paper are dried at 100° C. until the weight is constant. The paper is then extracted with hot water to remove soluble products, and again dried and weighed; the paper is then placed in a Soxhlet (fig. 65), and extracted with alcohol containing a few drops of acetic acid for one hour. The Soxhlet extraction apparatus (fig. 65) consists of a sort of test tube or cup with a syphon tube leading from the bottom. Near the top of the cup is a wide tube, and both this and the end of the syphon tube pass down and unite together in a sort of shank. The shank passes through a cork into a weighed flask containing the alcohol, and the mouth of the Soxhlet is connected to an upright condenser. This apparatus permits of a continual and automatic extraction of the paper in the following manner: The alcohol in the flask is kept boiling by immersion in a water-bath, the vapours pass up the broad tube and find their way into the condenser, where they are liquefied and drop back on to the paper. In this way the cup of the Soxhlet gradually fills up until it reaches a point on a level with the top of the syphon tube; at this moment the syphon begins to act and carries the alcohol back into the flask and with it any substances dissolved out of the paper. The alcohol in the flask continues to boil and the vapours rise and are condensed, dropping back on to the paper, so that the process repeats itself. The paper is thus extracted each time with fresh alcohol and the dissolved matters are carried over into the flask, where they collect. This apparatus has some disadvantages—the corks or stoppers of the flask and extraction apparatus are both exposed to the action of the solvent and consequently the extract is contaminated with soluble substances extracted from the corks or stoppers. This diffi-

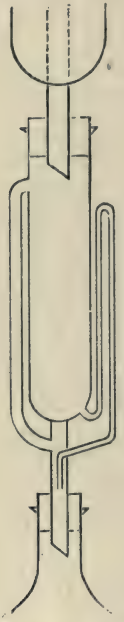


Fig. 65.—Soxhlet Extraction Apparatus.

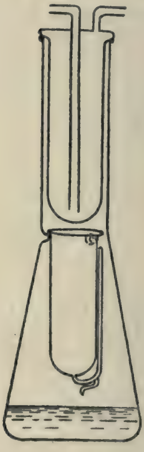


Fig. 66.

culty can be obviated by using ground-in glass joints, but these stick and break easily and are expensive.

The author has designed a new form of extractor (Fig. 66)[1] built entirely of glass. The extraction thimble which carries the syphon tube is detachable and normally rests on three small projecting pieces of glass, or it can be hung by a platinum wire from a glass hook fused on to the bottom of the condenser. The condenser is a single surface type but is found quite effective if 4 inches long and provided with a good current of water. When extraction is complete, the liquor from the flask is transferred to a tared flask for drying and weighing. This type of apparatus has the advantage over the older type that the extraction thimble is surrounded with vapour at the boiling-point so that the solvent it contains is almost at the boiling-point. Extraction under these conditions proceeds more rapidly than in the older form of apparatus where the condensed solvent is not surrounded by hot vapour but cools by radiation.

After an hour or so, the extraction may be considered complete, the flask removed, and the alcohol distilled off on a water-bath. To complete the drying, the flask is placed in an oven at 100° C., until the weight is constant. The increase in weight gives the weight of rosin extracted from the paper. The paper may also be removed, dried at 100° C., and weighed, the loss in weight giving again the matters extracted by alcohol.

The figure obtained by alcoholic extraction is usually too high as there may be other substances in the paper soluble in alcohol at the boiling-point. It is therefore proposed to extract the alcoholic extract with ether, as rosin is readily soluble in ether as well as alcohol. After evaporating off the alcohol, it is taken up in the same flask with 25 c.c. ether and 150 c.c. water. The liquids are transferred to a separating funnel, the aqueous layer drawn off and re-extracted with ether, and the ethereal extracts united. The ether is evaporated off in a tared flask and the residue dried in a water-oven and weighed. In this manner a certain amount of alcohol-soluble, but ether-insoluble, substances are excluded from the paper.

In place of the ether extraction the alcoholic extract can be titrated and the amount of rosin calculated by means of the factor 346 (see under Rosin).

---

[1] *Journ. Soc. Pub. Analysts*, April, 1913.

The percentage of rosin may also be determined by pouring the alcoholic extract into water in a Nessler tube. The opalescence or cloudiness produced is contrasted with that obtained by adding a known quantity of a solution of rosin in alcohol of 1 per cent. strength to another tube containing the same quantity of water until the same degree of opacity is obtained on looking down the tubes. The calculation is made in the same manner as in other Nesslerising tests.

Remarks.—Both the above tests are subject to an error, as the paper frequently contains substances soluble in alcohol other than the rosin added as size. An opalescence may be produced with the alcoholic extract when no size has been added in papers prepared from mechanical and sulphite pulps, as both these contain much of the natural resins of the original wood. Some colouring matters and other substances are also extracted with alcohol and precipitated with water. It will be seen that the figures obtained tend to be rather too high and that great care must be exercised in interpreting the experimental results.

Animal Size.—Gelatine may be extracted from a paper by means of hot water. A little of the paper is boiled with water in a test tube and the liquid poured off ; to the solution when cold a little tannin solution is added which reacts with the gelatine to produce a cloudy precipitate. On warming the liquid the precipitate coagulates in a characteristic manner, attaching itself to the sides of the test tube and leaving the liquid clear or almost so. This is important, as a solution of starch will also give a precipitate with tannin solution.

The percentage of gelatine in the sample of paper is accurately determined by means of the Kjeldahl test. This depends upon the fact that when heated with strong sulphuric acid the carbonaceous matter of the paper is entirely destroyed, while the nitrogen, of which gelatine contains a constant proportion, is converted into ammonia and retained by the sulphuric acid as ammonium sulphate. The procedure is as follows : One or two grams of paper are weighed out and introduced into a special long-necked flask made of resistant glass ; to this is added 10 c.c. concentrated sulphuric acid. Special acid for this purpose, free from nitrogen, can be obtained from chemical dealers. The flask and contents are heated over a small Bunsen flame and 4 grams of pure potassium sulphate added. At this stage the temperature may be increased to a point at which the contents almost boil, and is maintained until the reaction is complete. The first action of the sulphuric acid is to carbonise the paper, which dissolves to a dark liquid; this liquid gradually turns brown, then yellow, and finally becomes colourless, at which stage the reaction is complete. During the process much sulphur dioxide is evolved, so that it is best to carry out the reaction in a fume cupboard or where no annoyance will be caused. As soon as the contents of the flask are cold they are diluted with water and transferred to a large flask (fig. 67). One or two pieces of granulated zinc are added, and then 20 c.c. of a 50 per cent. solution of caustic soda. This will be sufficient to neutralise the excess of sulphuric acid and render the liquid alkaline. As soon as the soda is added, the bent delivery tube which also acts as a condenser, is replaced in the flask, and the end made dip into a small flask containing 20 c.c. $\frac{N}{10}$ H_2SO_4 (fig. 67). The large flask is now heated till the contents boil, when the ammonia gradually distils over and is condensed in the weak acid. The distillation should be continued briskly for twenty minutes or so, when the whole of the ammonia will have gone over. The contents of the small flask are now allowed to cool and the excess of acid determined by titration with $\frac{N}{10}$ alkali, using methyl orange as an indicator. The difference between the volume of alkali required and the volume of acid originally taken gives a volume of $\frac{N}{10}$ ammonia obtained from the gelatine in the paper. Multiplying this number of c.c. by 0·972[1] will give the percentage of "air-dry" gelatine in the paper, if one gram of paper be taken for analysis. A blank test should be made, using the same quantities of reagents and pure filter paper, which is free from nitrogen. If on distillation any acid is found to be neutralised, this must be subtracted from the acid neutralised in the above test.

---

[1] Taking 6·25 as the percentage of nitrogen, the factor for bone-dry gelatine would be 0·875. But making allowance for the moisture present in ordinary gelatine, the factor may be taken as 0·972.

As an example: on titrating after distillation, 13·4 c.c. $\frac{N}{10}$ alkali were required, while in the blank test 19·8 c.c. $\frac{N}{10}$ alkali. Then the percentage gelatine in the paper was $(19{\cdot}8 - 13{\cdot}4) \times {\cdot}972 = 6{\cdot}2$ per cent.

Casein.—As this substance is also nitrogenous and contains about the same percentage of nitrogen as gelatine, the amount contained in a sample of paper can be estimated by the above process for gelatine. As it is insoluble in water it cannot be removed like gelatine by hot water, but requires the aid of a little alkali such as sodium carbonate or ammonia. On carefully neutralising the alkali in the extract, casein is reprecipitated. As it is used mostly for coated papers, it is usually unnecessary to test for it except in these. The alkaline extract is precipitated with weak acetic acid and the precipitate washed with water and alcohol; it is then warmed with a mixture of two volumes glacial acetic acid and one volume strong sulphuric acid. A reddish-violet colour points to the presence of casein, while gelatine does not give any coloration.

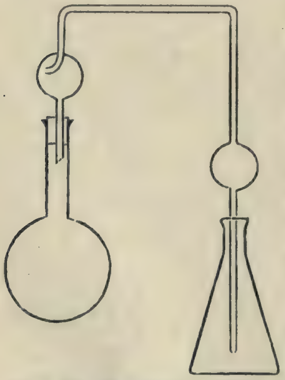


FIG. 67.—Kjeldahl Distilling Apparatus.

Starch.—Starch is tested for in paper by immersing strips in a very weak solution of iodine in potassium iodide, so weak as to be only straw-coloured. Papers containing starch are rapidly coloured blue, the larger the proportion of starch the more intense the colour. A rough estimate may be made of the proportion of starch by comparing the intensity of coloration obtained in this way with the paper under examination and comparing the depth of colour obtained with that produced in papers in the manufacture of which known amounts of starch have been added to the beater. Paper containing 5 per cent. of starch gives an intense dark colour. Dr. Wurster gives the following method for estimating the quantity of starch in a sample of paper. One gram is boiled for a few minutes with absolute alcohol containing a few drops of hydrochloric acid ; by this means rosin and other substances are removed. After washing with a little more alcohol the paper is dried at 100° C. and weighed. The paper is then boiled with equal volumes of alcohol and water, containing a few drops of hydrochloric acid, until it is no longer blued with iodine solution. The strip is then washed with alcohol, dried, and weighed. The loss in weight represents starch. The figure obtained is usually somewhat too high. Another process is that of Schumann and Hoyer. Five grams of the paper are extracted with rectified spirits in a Soxhlet. The alcohol is filtered off, care being taken not to lose any fibres, and the paper dried at 100° C. and weighed. The paper is then placed in a porcelain dish and treated with a fresh extract of malt at 60° to 70° C. until a test with iodine solution shows that all the starch has been removed; this usually takes half an hour. The paper is then washed with hot water to remove the residue of malt extract and sugar, dried at 100° C. and again weighed. The loss in weight represents the starch contained in the paper. In the place of malt extract pure diastase, the active ingredient of malt extract, may be used ; a small quantity is dissolved in a mixture of one part water and two parts glycerine, of which a few drops are sufficient for a test.

Reinke proposed to extract the starch by digesting the paper with ten times its weight of ½ per cent. lactic acid solution in an autoclave at 50 lb. pressure. The extract is boiled with dilute HCl to convert fully to sugar, and estimated with Fehling solution. A control test with the same paper free from starch is necessary, as cellulose itself yields some sugar under the treatment.

None of these methods is really satisfactory. Lutz, who made a critical study of them, prefers the last. Boiling with HCl or treatment with diastase dissolves other constituents besides the starch, and lactic acid hydrolyses some of the cellulose. Only in those cases where a control or blank can be made, using some of the same paper prepared without starch, is it possible to obtain reliable figures. Starch as determined by any of the methods described gives too high figures.

IDENTIFICATION OF COAL-TAR DYES.

In the case of papers dyed with coal-tar colours the following tables have been prepared by **Mr. H. A. Bromley** (see *The Paper-Maker*, 2nd February, 1914, p. 224).

The dye is first extracted from a given quantity of the coloured paper by treatment, first with alcohol and then with boiling water. The extracts, after mixing, are evaporated to a small volume, and, on addition of a saturated solution of common salt, the colouring matter is thrown out (salted out). The colouring matter thus precipitated is filtered off and dissolved in as small a quantity of water as possible.

A tannin reagent is prepared by dissolving 25 grams of tannin and 25 grams of sodium acetate in 250 c.c. of water. This reagent gives a precipitate with a basic, but not with an acid dye. The differentiation of the dyestuff is given in the tables on opposite page.

The third class of dyestuffs, namely, the substantive dyes, may be detected by adding a little sodium sulphate to the dye extract and immersing in the solution obtained a small piece of white mercerised cotton, which will be dyed in the presence of a substantive colour. For further details the reader is referred to *The Analysis of Dyestuffs*, by H. G. Green, published by C. Griffin & Co., 1915 edition.

SPOTS AND SPECKS IN PAPER.

The causes which may give rise to spots in paper are numerous. A careful chemical and microscopical examination will often reveal the fibre, foreign matter, or substance of which a spot is composed, so that its nature and origin can be traced.

Spots in paper can be classed under three heads (Dalén) :—

1. Spots which are ordinarily darker than the rest of the paper, but appear lighter when the sheet is held up against the light. To this class belong spots caused by grease, rosin, froth, particles of silicious matter, and knots which render the paper more transparent.

TABLE LXXX.

Dyes Precipitated by Tannin Reagent (Basic).

The aqueous solution is reduced with zinc dust and dilute hydrochloric acid, and a drop of the decolorised solution is spotted on filter paper. If the original colour does not quickly return on exposure to the air the spot is treated with a drop of chromic acid solution (1 per cent.).

Original colour quickly reappears.	Original colour appears very slowly or not at all without treatment with chromic acid.	Original colour does not return.
Azines, Oxazines, Thiazines, Acridines:— *Saffranines,* *Indulines,* *Indanthrenes, etc.*	Tri-phenyl-methane colouring matters. Basic Phthaleins:— *Rhodamines.*	[1] Auramine. Chrysoidine. Bismarck brown.

TABLE LXXXI.

Dyes not Precipitated by Tannin Reagent (Acid).

The aqueous solution is reduced by zinc dust and dilute hydrochloric acid, and a drop of the decolorised solution is spotted on a filter. If colour does not quickly return on exposure to air the spot is treated with a drop of a solution containing 1 per cent. chromic acid and 5 per cent. sulphuric acid, warmed over a flame and held in the vapour of ammonia.

The Solution is Decolorised.					Solution is not Decolorised or only very slowly.
Original colour quickly reappears on exposure to air. **Sulphonated azines, oxazines and thiazines.**	Original colour does not reappear or only slowly on exposure to air but does so with chromic acid.		Original colour does not reappear at all. **Azo or Nitro compounds.**		Quinoline Yellow.
Sulphide dyestuffs and soluble nigrosines, etc.	Acidify aqueous solution and shake with ether.		Heat solid colour on platinum foil.		
	Ether extracts colour.	Ether does not extract colour.	Nitro-compounds deflagrate with coloured fumes.	Azo compounds burn but do not deflagrate.	
	PHTHALEINS:— Eosines, etc.	Sulphonated Tri-phenylmethane colours: Acid magenta, Acid violet, Alkali blue, Soluble blue, Fast green, Acid green, etc.			

---

[1] The reduced solution gives a violet colour on warming spot.

2. Spots which always appear darker than the rest of the paper, whether held up to the light or not. These spots are caused by opaque substances, such as particles of iron, bronze, lead, coal, mineral or coal-tar colour, sealing wax, rubber and fibrous residues, such as splinters of mechanical wood, sheave of flax or hemp, cotton seed hulls, and mildew stains.

3. Spots which are at first imperceptible or almost so, but which subsequently make their appearance when the paper is further treated, *e.g.* super-calendered, coated, parchmentised or sensitised for photographic purposes. These spots may be caused by knots, residues of bleach or calcium sulphite, particles of starch, iron, grease, sand, fillers or mechanical wood.

This formidable list demonstrates the varied origin and nature of spots, from which it follows that their identification is a difficult operation requiring considerable care and skill. In what follows the methods for examining spots in a number of cases are given.

Transparent Spots.—Rosin Spots disappear or lose much of their transparency on treatment with alcohol or ether. Small portions of the paper containing the spots are removed, marking the position of each spot with a pencil. The pieces of paper are then warmed with a little alcohol or ether in a test tube, and examined again after pouring off the solvent, and drying. Rosin spots are often associated with other substances: on dissolving out the rosin a hollow is formed in the surface of the paper. This, on further examination, has usually a dark appearance due to the presence of a substance containing iron, and white particles of fillers may also be found.

The rosin spot is derived either from the size or particles of resin in the original wood pulp (in the case of wood pulp papers). In the latter case the spots are usually larger, more irregular in shape and more difficultly soluble in alcohol or ether; they also contain at times particles of calcium sulphite or sulphate.

Grease Spots are similar in appearance to rosin spots, but the edges are somewhat better defined and they are not dissolved by cold alcohol. Ether dissolves them readily, leaving a dark spot containing a residue of iron or copper. The paper is moistened with dilute hydrochloric acid and then immersed in a weak solution of potassium ferrocyanide. Iron spots give a blue mark;

spots containing copper a chocolate-coloured mark, due to the formation of the ferrocyanides of iron and copper respectively. The grease spots usually have their origin in the lubricating oil from the bearings of the beater rolls.

Froth produces spots in paper which vary in appearance, but are usually characterised by a slight hollow surrounded by a raised ring: after passing between the calender rolls this ring is often more transparent than the centre portion of the spot and sometimes appears a different colour. Froth spots may contain rosin when the size is the cause of the trouble.

Sand or micaceous particles (fig. 25) produce semi-transparent spots which are not very noticeable so long as they remain in the paper. When the paper is calendered they fall out, leaving very distinct holes or hollows with sharply defined edges. Sand spots sometimes occur in pairs caused by a particle of hard substance on a calender roll: the paper will be marked twice as it passes over and under the roll, the two marks being close together but not coinciding owing to the paper stretching in the process. The particle is removed from the paper with a needle and examined microscopically for purposes of identification. Silicious particles are very resistant to chemical reagents, with the exception of hydrofluoric acid.

Knots consist of balls of fibres or portions of broke which have escaped thorough disintegration and form little lumps or raised spots in the paper which are not very noticeable until after passing the calender rolls where the greater pressure on the raised spots compresses them so that they become transparent. In general appearance they resemble rosin spots, but are not removed by ether, and swell up when treated with weak soda. To trace their origin they are examined microscopically to ascertain the nature of the fibre of which they are composed, in particular, whether they consist of the same fibres that form the bulk of the paper. Occasionally they may be traced to the addition of waste paper which has not been thoroughly disintegrated or to the silicious cells occasionally found in straw pulps.

Opaque Spots—Iron Spots.—These are detected with ferrocyanide solution as already described. In appearance they vary considerably, and may consist of metallic iron, iron oxide (rust), with or without grease. Particles of metallic iron are very minute, and form black points which are not very noticeable till the paper is moistened for calendering or stored a trifle damp. Particles of metallic iron are magnetic, *e.g.* are attracted by a magnetised needle. This serves to identify them. They are sometimes caused by lowering the beater rolls too suddenly.

Iron oxide spots are brittle and non-magnetic. They originate in iron water pipes or tanks, and consequently they frequently contain lime salts as well as iron. The rust gradually accumulates on the surface and then scales off in brittle pieces.

Sometimes the iron is in a soft powdery form with rosin or grease, and is examined as described under rosin and grease spots. The iron may be derived from the water or from the bearings of some part of the machine, when rust spots appear which are mostly confined to the surface of the paper.

In all cases a careful microscopic examination is made of the spot, which is probed with a needle and otherwise manipulated to ascertain its nature.

Bronze Specks form minute glistening particles which cannot usually be detected until the paper has passed the calender rolls. Their appearance under a low power is extremely characteristic, forming fern-like growths radiating from a dark centre. With large spots the peculiar structure can be seen with the naked eye. They may originate either from bronze beater bars or from sulphite pulp, in the latter case probably from partially corroded bronze fittings of the sulphite boilers. As bronze contains copper, a chocolate colour is produced with potassium ferrocyanide solution.

Lead particles from the linings or lead pipes in sulphite boilers have also been known to give rise to spots in paper.

Coal or coke particles form black spots in paper. They are identified by general appearance, resistance to acid, and the white ash left on burning.

Colours.—Both mineral and coal-tar colours may produce spots, little lumps of colour, the particles of which have hung together. They are found mostly in coloured papers, or as particles of ultramarine or other blue used in toning white papers. The powdery consistency of the spots is ascertained by probing with a needle and the identification of the colour may be made, as described in Chapter V.

Sealing Wax from waste papers occasionally forms spots. The colour of the red wax is characteristic, but black or brown wax is more difficult to identify.

Rubber particles are characteristic in appearance and properties if the particles are large enough to examine for elasticity and resiliency. The particles may be picked out and the following delicate test applied: Nitric acid is poured on the particles in a test tube which is placed in a beaker of hot water about 60° C. for an hour. The water in the beaker is then heated to boiling for a few minutes. The nitric acid solution is now poured off into another test tube containing a little strong caustic soda solution (10 c.c. caustic soda solution, 1 in 4 for every c.c. nitric acid used) when a yellow-coloured liquid is obtained on diluting and filtering if rubber be present.

Splinters of mechanical wood, sheave or cotton seed hulls, are identified microscopically; they give the colour reactions of ligneous fibre.

Foreign Particles in Pulp and Half-stuffs.—Half-stuffs may contain particles of substances, such as are described in the foregoing paragraphs, which give rise to spots in paper. The methods of identification are those already described; *e.g.* mechanical pulp may contain gritty pieces of sandstone from the grinders; sulphite pulp, particles of resin from the wood; and rag pulp, any of the various odd substances derived from buttons, seams, wire-hooks, etc., in the original rags.

Moulds and Mildew.—Both paper and pulp in moist condition are liable to develop growths of moulds. Paper is so strongly heated when passing over the drying cylinders that moulds and their spores are destroyed. Nevertheless, fresh growths will always appear when the circumstances are favourable to their growth. The gelatine in tub-sized papers forms a very suitable medium if sufficiently moist. It is, however, mostly in the case of pulps, and especially mechanical pulp, that cases of mould growths have to be investigated. Mechanical pulp is rather susceptible in this respect, as it is stored moist and contains much of the albuminous matter of the original wood. The dark spots are examined microscopically, when the low form of vegetable growth will be usually found to consist of branching rods, some of which carry spores. The globular sacs of *mucor mucedo*, sometimes burst with the spores gone, are characteristic. Pulp attacked by such growths gives a much larger water soluble extract than sound material. The extract strongly reduces Fehling solution.

CHEMICAL IMPURITIES IN PAPER.

Residues of bleach, antichlor or free acid have a tendency to rot paper and cause it to go back in colour. Of course, every precaution is taken to see that pulp in the beater is free from all residues of bleach liquor before emptying, but even if they find their way into the finished paper they soon disappear on account of their chemically reactive nature. In most cases when tests are made to detect chemical residues of bleach negative results are obtained, in particular chlorine and hypochlorites are rapidly decomposed; the damage is done and the free chlorine vanishes before there is time to apply the test. In such cases the chlorine will be converted into chlorides which may be extracted with water and tested for with a silver nitrate solution. If any one is desirous of testing paper for free chlorine, it should be extracted with cold water and the solution tested with potassium iodide and starch liquor; even a trace of free chlorine will produce a blue colour.

An excess of antichlor brings down the colour of the paper, but when tested for, it is not usually to be found, for the reasons already given. The best procedure is to make a cold-water extract with, say, 2 grams of the paper and titrate with a $\frac{N}{100}$ iodine solution, using starch as an indicator. A blank test should also be made with the same quantity of distilled water in a beaker which has stood alongside of that containing the paper. It will be found that even distilled water contains substances which combine with iodine and decolorise it, and the difference between the two titrations will represent the iodine absorbed by matters extracted from the paper. Even with this test it is dangerous to draw conclusions until experience has been gained in the examination of a number of papers.

Free acid in paper is very destructive, as the cellulose of the fibre is gradually acted on and rendered brittle.

The paper is tested by the application of a suitable indicator; as, however, an excess of alum is always used in sizing, and as alum itself is of an acid nature and reacts acid to indicators such as litmus, it follows that papers giving an acid reaction to litmus do not necessarily contain free acid in the above sense, but merely an excess or residue of alum. Methyl orange is affected to a lesser extent than litmus and is a more suitable indicator to use for the purpose. Congo red is another indicator which is certainly neutral to alum; it is turned blue by mineral acids. The paper is extracted with hot water and the solution treated with a drop of methyl orange solution. Free acid will cause the faint yellow colour to change to an orange or reddish shade. A blank test should always be made with a similar quantity of distilled water and the colours of the two liquids compared. Under these conditions any difference in colour between them is readily detected. If the paper is white or only faintly coloured, a drop of the indicator may be placed on the surface and left to stand for a short while, a similar drop being placed on a piece of paper known to be free from acid. Tests with Congo red are carried out in exactly the same manner, but the test is rather less sensitive. It is sometimes useful to estimate the acidity of the paper including any alum or other acid substance which it may contain. For this purpose a known weight of paper is extracted with hot water and the extract titrated with $\frac{N}{10}$ alkali, using litmus as an indicator. The liquid is boiled from time to time during titration to drive off carbonic acid. The extract of some papers, however, reacts alkaline, and the alkalinity may be similarly determined by titration with $\frac{N}{10}$ acid and litmus. At one time it was customary to prescribe absence of chlorine and free acid in papers, as, for instance, in the Government contracts in Germany. As a result of careful investigation, the practice has been discontinued, the officials of the Government laboratory preferring to base their opinion on other physical and chemical tests.

Papers for Wrapping Polished Metal.—Certain residues in wrapping paper will corrode polished steel, silver, and silver-plated goods. Of course, paper intended for such purposes must contain no free acid; further, it should contain no sulphides, sulphites, or other substances likely to tarnish the goods. The paper is subjected to a careful examination, as already described. The titration of a cold-water extract with iodine solution will give information as to the presence of soluble sulphides and sulphites, as these react with iodine. The presence of sulphides may also be detected by warming the paper with weak sulphuric acid, when sulphuretted hydrogen is given off and detected by its smell, or by bringing a piece of filter paper impregnated with silver nitrate solution over the mouth of the test tube containing the paper, when a metallic deposit will be formed. As to the origin of these sulphur compounds, it should be remembered that sulphite pulp frequently contains sulphur residues derived from sulphite liquors, and further that sulphur compounds tend to be precipitated on the fibre, when thiosulphate is used as an antichlor.

Discoloration of Paper.—In papers containing mechanical wood pulp the tendency to discoloration is inherent in the raw material itself and common to all such papers. It need not, therefore, be further considered here.

On the other hand, papers free from mechanical pulp, even rag papers at times, show a marked tendency to turn yellow with age. This subject has been investigated by Klemm, who attributes the "yellowing" to the presence of certain compounds of iron with resinous or fatty matters. The tendency to discoloration is proportional to the percentage of these organic iron compounds in the paper. To estimate this percentage a known weight of paper is extracted with a mixture of one part alcohol and two parts ether in a Soxhlet. The residue from the evaporation of the extract contains the organic iron compounds, while the inorganic iron compounds are left in the paper. The residue is burnt to ash in a crucible, taken up with acid and the iron estimated by Nesslerising (see Iron in Water).

For rough tests the iron organic compound may be dissolved out with 1 per cent. caustic soda solution, 1 gram of paper being heated with 5 c.c. in a test tube; the yellowish liquor is poured off into another test tube, acidified with nitric acid and tested for iron colorimetrically.

CHAPTER VIII.

SIZES AND WEIGHTS OF PAPERS.

To determine the weight per ream special paper scales are constructed. Scales are sold to determine the weight per ream either from (*a*) the weight of a single sheet; (*b*) the weight of a piece of the paper cut four inches square.

The dials of these machines are usually provided with two scales, giving the weights per ream of 480 and 500 sheets.

Of course, any suitable balance or scales can be used, and the weight found for the sheet multiplied up by the number of sheets per ream.

The accompanying tables give the ordinary sizes of papers :—

TABLE LXXXII.

SIZES OF PAPERS.

Drawing Papers.

	Sizes.
Emperor	72 × 48
Antiquarian	53 ,, 31
Double Imperial	46 ,, 30
,, Elephant	40 ,, 27
,, ,,	40 ,, 26¾
Atlas	34 ,, 26
Colombier	34½ ,, 24
,,	34½ ,, 23½
Imperial	30 ,, 22
Elephant	28 ,, 23
Super Royal	27¼ ,, 19¼
,, ,,	27 ,, 19
Royal	24 ,, 19
Medium	22 ,, 17½
Demy	20 ,, 15½
Foolscap	16¾ ,, 13¼

TABLE LXXXII. (*continued*).

CHART PAPERS.

	Sizes.
Antiquarian	53 × 31
Double Elephant	40½ ,, 27
Atlas	34 ,, 26
Colombier	35 ,, 24
Imperial	30 ,, 22
Super Royal	28 ,, 20
Royal	25 ,, 20
Demy	22½ ,, 17¾
,,	22½ ,, 17½

PLATE PAPERS.

	Sizes.
Antiquarian	53 × 31
Double Imperial	44 ,, 30
,, Elephant	40 ,, 27
,, ,,	40 ,, 26¾
Atlas	34 ,, 27
,,	34 ,, 26
Colombier	35 ,, 24
,,	34½ ,, 23½
Imperial	30 ,, 22
Elephant	28 ,, 23
Super Royal	28 ,, 20
Royal	25 ,, 20
Medium	23½ ,, 18½
Demy	22½ ,, 17¾
,,	22 ,, 17½
Foolscap	17 ,, 13½

ACCOUNT BOOK AND WRITING PAPERS.

	Sizes.
Atlas	33½ × 26½
Imperial	30 ,, 22
Super Royal	27 ,, 19¼
Royal	25 ,, 20
,,	24½ ,, 20
,,	24 ,, 20
,,	24 ,, 19¼
,, Copying	24¾ ,, 20¾
,, Foreign Post	23½ ,, 19¼
Medium	23 ,, 18
,, Copying	22½ ,, 18½
,,	22½ ,, 18
,, Foreign Post	22¼ ,, 17½
,,	22 ,, 17½
,,	22 ,, 17
Demy	20 ,, 15½
,,	19¾ ,, 15½

TABLE LXXXII. (*continued*).

	Sizes.
Extra Large Post	22½ × 17¾
Large Post	21 ,, 16½
,,	20¾ ,, 16½
Post	19 ,, 15¾
,,	19 ,, 15¼
,,	18¾ ,, 15¼
Pinched Post	18½ ,, 14¾
,,	18½ ,, 14½
Foolscap	17 ,, 13½
,,	16¾ ,, 13¼
,,	16½ ,, 13¼
Pott	15¼ ,, 12½
,,	15 ,, 12½
Copy	20¼ ,, 16
,,	20 ,, 16
Sheet and ⅓ Foolscap	22 ,, 13½
,, ,,	22 ,, 13¼
,, ½ ,,	24½ ,, 13¼
,, ½ Pott	22½ ,, 12½
Double Large Post	33½ ,, 21
,, Post	30½ ,, 19
,, Foolscap	27 ,, 17½
,, ,,	27 ,, 17
,, ,,	26½ ,, 16¾
,, ,,	26½ ,, 16½
Double Pott	25 ,, 15

FOREIGN POSTS AND COPYING.

	Sizes.
Medium	22¼ × 27½
Royal	23½ ,, 19¼
Double Foolscap	27 ,, 17
Medium Copying	22½ ,, 18½
Royal ,,	24¾ ,, 20¾

CARTRIDGE PAPERS.

	Sizes.
Elephant	31 × 22
,,	28 ,, 23
Imperial	30 ,, 22
Engineering	30 ,, 22
Royal	25 ,, 20
Demy	22½ ,, 17¾
Copy	20 ,, 16½
Double Demy	35½ ,, 22½
,, Crown	30 ,, 20
Ammunition	24 ,, 19
Double Foolscap	27 ,, 17
Cartridge	26 ,, 21

TABLE LXXXII. (*continued*).

BLOTTING PAPERS.

	Sizes.
Royal	25 × 20
,, Treasury	24 ,, 19
Demy	22½ ,, 17¾
Post	19 ,, 15¼
Double Foolscap	26½ ,, 16¾

MISCELLANEOUS PAPERS.

	Sizes.
Royal Drying	24 × 19¼
Tissue Double Crown	30 ,, 20
,, Demy	22½ ,, 17¾
Filtering Paper	24 ,, 24
Copying Medium	22½ ,, 18½
,, Double Foolscap	27 ,, 17
,, Royal	24¾ ,, 20¾
Long Elephant	30 × 12 yards
,,	22½ ,, 12 ,,

PRINTING PAPERS.

	Sizes.
Double Demy	35 × 22½
,, Crown	30 ,, 20
,, Medium	37 ,, 23½
,, ,,	36 ,, 23
,, Royal	40 ,, 26
,, ,,	40 ,, 25
,, ,,	38 ,, 24
,, Foolscap	27 ,, 17
,, Large Post	33 ,, 21
,, Post	31½ ,, 19½
Sheet and ½ Post	23½ ,, 19½
Double Copy	33 ,, 20
,, Pott	25 ,, 15½

PRINTING PAPERS—(*continued*).

	Sizes.
Imperial	30 × 22
Elephant	30 ,, 23
Super Royal	28 ,, 20
Royal	26 ,, 20
,,	25 ,, 20
,,	24 ,, 19
Medium	23½ ,, 18½
Demy	22½ ,, 17¾
Music Demy	20¾ ,, 14⅜
Demy and Medium	various sizes.

TABLE LXXXII. (*continued*).

BROWN, SUGAR, DOUBLE SMALL HANDS, ETC.

	Sizes.
Casing	48 × 40
,,	48 ,, 38
,,	48 ,, 36
,,	46 ,, 36
Double Nic-a-Nee	56 ,, 45
Nic-a-Nee	45 ,, 28
Double Imperial	45 ,, 29
Imperial	30 ,, 23
,,	29 ,, 22½
,,	29 ,, 22
Elephant	34 ,, 28
,,	34 ,, 24
Double 4 Pound	34 ,, 23
,,	33 ,, 21
,,	31 ,, 21
Bag Cap	24 ,, 20
,,	24 ,, 19
Kent Cap	22 ,, 18
,,	21 ,, 18
Double Bag Cap	40 ,, 24
Havon Cap	26 ,, 21
Cartridge	26 ,, 21
Copy	20 ,, 16¼
Extra Double Crown	32 ,, 22
Large Imperial	32 ,, 24
Plutarch	36 ,, 26
Saddleback	45 ,, 36
Double Small Hands	30 ,, 20
,, ,,	29 ,, 19
,, ,,	28 ,, 18
,, ,,	27 ,, 17
,, ,,	24 ,, 16
,, ,,	23 ,, 15
,, ,,	22 ,, 14

Conversion of weight per ream (in pounds) to grams per square meter, and vice versâ.

For these calculations we have the following data:—

Weight per ream in pounds *or* weight per square meter in grams.

Area of sheet in square inches obtained by multiplying the breadth by the length.

Number of sheets per ream.

A factor for converting pounds per square inch to grams per square meter = 703245.

To calculate grams per square meter from ream weight :—

$$\frac{\text{Ream weight} \times 703250}{\text{No. of sheets per ream} \times \text{length of sheet} \times \text{breadth of sheet}} = \text{grams per square meter.}$$

To calculate ream weight in lb. from weight in grams per square meter :—

Grams per sq. meter × No. of sheets per ream × length of sheet × breadth of sheet ÷ 703100 = pounds per ream.

Example.—What is the weight in grams per square meter when a ream (500 sheets) demy (17½ × 22½) weighs 16 lb. ?

$$\frac{16 \times 703100}{500 \times 17{\cdot}5 \times 22{\cdot}5} = 57{\cdot}14 \text{ grams per sq. meter.}$$

Conversion of weight per ream of paper of one size to that of another.

Divide the weight per ream by the area of the sheet, and multiply by the area of a sheet of the size required.

Example.—What is the weight per ream double elephant (40 × 27) when the weight per ream demy (17½ × 22½) is 16 lb. ?

$$16 \times \frac{40 \times 27}{17{\cdot}5 \times 22{\cdot}5} \times 43{\cdot}89 \text{ lb.}$$

CHAPTER IX.

PAPER TRADE CUSTOMS.

CONTRACT NOTE FOR WOOD PULP

(AS ORIGINALLY ADOPTED BY THE BRITISH WOOD PULP ASSOCIATION AND THE PAPERMAKERS' ASSOCIATION).[1]

M ________________________________

____

We have this day ________________________________

____

Quantity and Description of Goods :—

Mode and Place of Delivery :—

Time of Delivery :—

Price :—

Terms of Payment :— (Cash before delivery if required.)

Remarks :—

Subject to the conditions printed below.

____

____

________________ 19 ____

---

[1] There is at present (1917) no official Contract Note for Wood Pulp.

CONDITIONS.

1. *Packing and Weight.*—The pulp to be packed in covered bales of declared uniform weight, or a specification to be given stating the weight and number of each bale. The price named is per ton of 2240 lb. (= 1015 kilos) gross for net.

2. *Definition of "Air-Dry."*—By air-dry weight is understood 90 parts absolutely dry pulp and 10 parts water.

3. *Quantity.*—Should the buyers question the quantity of pulp invoiced, the dispute shall be forthwith determined by an agreed public analyst of acknowledged good standing. The analyst shall at the consumer's mill, or at any public wharf in the United Kingdom, forthwith sample and subsequently test the pulp, and determine the quantity to be reinvoiced (provided the difference exceeds 0·5 per cent.). The samples to be drawn by the analyst from accurately weighed, intact bales, from near the top, centre, and bottom, of not less than 2 per cent. nor more than 4 per cent. of the bales—but not less than five to be sampled. The costs to follow the result, and the award to be final.

4. *Quality.*—Any dispute as to quality other than such as concerns excess moisture or short weight, as provided for under Clauses 2 and 3, shall be referred to arbitration, as below provided. Should the delivery of pulp be found, upon arbitration, not to be reasonably equal to the sample sold upon, it shall be left to the arbitrators or umpire to decide whether or not the pulp shall be rejected or taken at an adequate allowance.

5. *Force Majeure.*—The buyers or sellers may suspend deliveries under this contract pending any contingency beyond their control, which prevents or hinders the manufacture of paper or delivery of pulp, *viz.:* Act of God, war, strikes, lock-outs, drought, flood, accidents, total or partial fire, obstruction of navigation by ice at the port of shipment (excepting the Baltic and St. Lawrence ports), and loss and detention at sea, or the like. The sellers, or buyers, as the case may be, shall give prompt notice to the other party of the cause and commencement of such suspension, and also when it ceases to have effect, and deliveries shall be resumed as soon as practicable, and in the case of deliveries spread over periods of time, they

shall, when resumed, be made at the same rate as provided in this contract, unless otherwise mutually agreed.

6. *Breach of Contract.*—Except as to cases within Clauses 4 and 5, where the buyers refuse to take delivery of pulp during the currency of this contract, the goods cannot be afterwards claimed, but may be sold by the sellers, after due notice, for the buyers' account. On the other hand, failure of the sellers to make delivery entitles the buyers, after due notice, to purchase against the sellers for their account. Each delivery under this contract is to be treated as a separate contract, and failure to give or take any delivery shall not avoid the contract as to other deliveries.

7. *Default or Bankruptcy.*—If the buyers make default in any payment or become subject to the bankruptcy laws, the sellers may, at their option, refuse to make further deliveries.

8. *Time Limit.*—All claims, of whatever nature, must be made in writing within fourteen days after the delivery of the consignment at the consumer's mill, wharf, or station in the United Kingdom, and no claims posted after that period will be recognised.

9. *Arbitration.*—Except as provided for in Clause 3, all disputes under this contract shall be settled in the United Kingdom by arbitration under the Arbitration Act, 1889. Each party to appoint an arbitrator, who upon questions of quality shall be an expert in paper or pulp, and they to appoint their umpire before proceeding on the reference. If either party fail to appoint their arbitrator within days of notice in writing requiring him to do so, the arbitrator appointed by the other party shall act for both parties, and his award shall bind both parties as if he had been appointed by consent.

PAPER TRADE CUSTOMS.

Paper trade customs codified by the Papermakers' Association of Great Britain and Ireland (Incorporated), the Scottish Papermakers' Association, and the Association of Wholesale Stationers. 1st January, 1906.[1]

---

[1] No alterations have been made to date (1917).

The following are the recognised customs of the trade relative to paper-making, provided that no agreement to the contrary has been made at the time of the order between the vendor and purchaser.

I. SALE.

Paper is sold either at a price per ream, based upon its nominal weight, or at the weight by the pound, packed in reams or in reels. Wrapping paper is sold at scale weight.

Machine-made Papers :—

1. A ream of paper, unless otherwise specified, contains 480 sheets.
2. A "Perfect" ream for printing papers contains 516 sheets.
3. A ream of envelope paper contains 504 sheets.
4. A ream of "News" contains 500 sheets.
5. An "Insides" ream contains 480 sheets all "Insides," *i.e.* 20 good or inside quires of 24 sheets.
6. A "Mill" ream contains 480 sheets, and consists of 18 "Good" or "Insides" quires of 24 sheets each, and 2 "Outsides" quires of 24 sheets each.
7. Reams are classed as "Good," "Retree," and "Outsides." The price of "Retree" is 10 per cent., and of "Outsides" 20 per cent. lower than that of "Good."

Hand-made Papers :—

8. A "Mill" ream "Good" or "Retree" contains 472 sheets and consists of 18 "Insides" quires of 24 sheets each, and 2 "Outsides" of 20 sheets each.
9. An inside ream "Good" or "Retree" contains 480 sheets, and consists of 20 "Insides" quires of 24 sheets each.

In all cases the "Outsides" quires are placed one at the top and one at the bottom of the ream.

II. VARIATIONS IN WEIGHT.

1. In printings, writings, etc., the average variation in substance of any ream must not exceed 4 per cent., either above or below the ordered substance.

In greys, caps, Manilas, browns, coloured printings, etc., the average variation in substance of any ream must not exceed 5 per cent. either above or below the ordered substance.

2. In news, printings, writings, etc., the average variation in substance of any reel must not exceed 5 per cent. above or below the ordered substance.

In the case of paper on reels, claims for short length can only be made when the shortage exceeds 5 per cent., and then only for the amount of any excess over and above such 5 per cent., unless special arrangements to the contrary are made.

In greys, caps, Manilas, browns, coloured printings, etc., the average variation in substance of any reel must not exceed 6 per cent. above or below the ordered substance.

3. But for all papers of substance under 6 lb. demy (17½ by 22½) and above 50 lb. demy, the actual weight may vary 8 per cent., either over or under.

4. Payment for paper in reels, according to the printed or manufactured results, cannot be claimed by the purchaser.

III. Variations in Measurement.

1. The variation in measurement of paper in reams must not exceed one-half per cent., either above or below the ordered measurement, but in no case shall the margin of variation exceed one-quarter inch, or be less than one-eighth of an inch.

2. The width of paper in reels must vary more than ½ per cent.

N.B.—Sections II. and III. are not applicable to hand-made paper.

IV. Special Makings.

1. For makings of special weight, size, tint, water-mark, etc., not having a regular sale in the market, the buyer is to take at full price any excess not exceeding 10 per cent. above the quantity ordered, including a reasonable proportion of "Retree."

2. Where a maximum quantity is stipulated for when ordering, the order is considered duly executed if it amounts to not less than 90 per cent. of the stipulated quantity.

V. MATERIALS.

1. Unless otherwise expressly stipulated in the order, the maker is free as to what material he shall use.

VI. WRAPPING UP.

1. The weight of necessary wrappers and string for reams and reels is to be included in the chargeable weight of the paper.

VII. MODE OF PAYMENT.

1. The customary terms of payment are:—

A monthly account to run from the 20th of one month to the 19th of the next, payable during the succeeding month; thus goods invoiced from the 20th January to the 19th February, shall be payable during March.

VIII. RETURN EMPTIES.

1. Carriage on returned empty frames, centres, boards, boxes, packing, etc., is payable by the customer returning the same, unless special arrangements to the contrary are made.

IX. EXCESS CARRIAGE.

1. That the excess carriage charged by the railway companies on Smalls be paid by the purchaser.

X. MARKING REAMS.

1. The actual weight ordered shall be marked on each ream at the mill.

XI. LIMIT OF TIME.

1. The limit of time for a mill to hold stock to order of the purchaser shall be six months from the date when the paper is advised as ready for delivery, such date not being earlier than that specified on the order, after

which it shall be invoiced, and shall therefrom become the property of the purchaser, and remain at his sole risk and expense, and shall be paid for within thirty days of invoice.

XII. DANDIES AND MOULDS.

1. DANDIES.—In all cases the purchaser shall pay for the dandy or moulds forthwith, but the maker shall allow an extra 2½ per cent. off the invoice for each delivery of paper made from such dandy until the cost of same is extinguished, after which it shall become the property of the maker. If after an interval of three years no further order has been received, the maker shall be at liberty to take out the water mark and make use of the frame as his property after giving thirty days notice, provided, nevertheless, that the purchaser shall have the right of retaining the dandy or moulds by refunding one-half of the extra discount of 2½ per cent., allowed in respect of the cost.

Note.—The trade customs as codified in 1899 are hereby cancelled.

CANADIAN TRADE CUSTOMS.

The following rules have recently been agreed to by Canadian manufacturers of book, litho., and fine papers; they also apply to other sorts of paper. It will be seen that the rules closely follow those adopted in Great Britain and the United States:—

1. All prices quoted shall be based on paper in rolls, without heads or rods; or on paper interlapped in bundles. The "standard" shall be on a minimum weight basis of 24½ by 36½—36 pounds—500 sheets to the ream for "machine-finished" papers, and 24½ by 36½—40 pounds—500 sheets to the ream for "super-calendered" papers. The average variation from the ordered weight is not to exceed 4 per cent. above or 4 per cent. below such ordered weight, paper within this range of variation to constitute a good delivery. All paper is to be billed at the ordered weight; no allowance shall be made by any manufacturer unless a variation is established in excess of 4 per cent.

2. No paper to be made one weight and stencilled another, *i.e.* paper must be marked by the manufacturer the "ream weight" ordered, and there shall be no evasion by substituting letters or symbols for figures of weight. For all paper of a weight below the "standard" (as per clause No. 1) of 24½ by 369—36—500 machine-finished paper down to and including 28 pounds in weight, 5 cents per 100 pounds extra shall be charged for each pound per ream below the "standard" weight, and for all "super-calendered" paper below the "standard" weight of 24½ by 26½—40—500 down to and including 32 pounds in weight, 5 cents extra per 100 pounds for each pound per ream shall be charged; and for machine-finished paper under 28 pounds and for "super-calendered" paper under 32 pounds, 10 cents extra per 100 pounds for each pound per ream below the weights of 28 pounds and 32 pounds respectively shall be charged, *e.g.* when paper is ordered 24½ by 36½—500 pounds machine-finished at, say, 5 cents per pound (5·40), five and four-tenths shall be paid for such paper when made 28 pounds to the ream. If ordered 26 pounds per ream the price to be paid shall be (5·60) five and six-tenths per pound, and so on.

3. For paper packed flat in skeleton frames there shall be a charge of 10 cents per 100 pounds, and for paper packed flat in cases or solid boards top and bottom there shall be a charge of 15 cents per 100 pounds.

4. For paper cut or trimmed two sides there shall be an extra charge of 10 cents per 100 pounds, and for paper cut or trimmed three or four sides there shall be an extra charge of 15 cents per 100 pounds. A further charge of 10 cents per 100 pounds per cut is to be made for every cut on all book and/or litho. papers when cut to a smaller size than 18 by 24.

5. Wrappers and twine are in all cases, on both sheet and roll papers, to be included in the weight of, and are to be charged for at the price of the paper ordered.

6. Roll paper shall be charged at the gross "scale weight," including cores; manufacturers will bear the cost of freight on cores, heads, and rods returned to the mill in good condition; but when cores are returned no allowance shall be made for any paper remaining on the cores so returned, except that an allowance may be made for clean white waste, at the current market price of the waste, *i.e.* cores shall be credited at the full selling price

of the paper that has been wound thereon, when the cores are returned stripped and in good order.

7. No allowance or payment shall be made by any manufacturer for any cases, solid tops or bottoms, or for skeleton frames returned.

8. Terms of payment shall be three months from date of invoice, or 3 per cent. may be allowed for cash in thirty days from date of invoice.

"TRADE CUSTOMS" OF THE BOOK MILLS IN U.S.A.

1. Terms of all sales to be on a basis of cash in thirty (30) days, less three per cent. (3 per cent.).

2. Minimum basis of weight for standard papers to be as follows :—

Machine finished, 24 by 38—40 pounds to 500 sheets.

Super-calendered, 24 by 38—45 pounds to 500 sheets.

For lighter weight papers the extra cost of manufacture to be added according to weight, estimated as follows :—

On machine-finished paper for each pound cut below 24 by 38—40 pounds to 500 sheets, to and including 24 by 38—30 pounds to 500 sheets, 5 cents per 100 pounds additional.

For each pound cut below 24 by 38—30 pounds to 500 sheets, 10 cents per 100 pounds additional.

On super-calendered paper for each pound cut below 24 by 38—45 pounds to 500 sheets, to and including 24 by 38—35 pounds to 500 sheets, 5 cents per 100 pounds additional.

For each pound cut below 24 by 38—35 pounds to 500 sheets, 10 cents per 100 pounds additional.

3. In all cases, on both sheets and roll orders, wrappers and twine to be charged at the price of the paper.

4. Rolls to be charged at the gross weight, including cores.

5. No printed waste to be returned and no paper taken back unless damaged before delivery ; and in case customer desires to make claim for damaged paper, same must be reported immediately to the manufacturer in order that the paper may be inspected before it has been printed.

6. In billing paper no allowance to be made for waste.

7. Manufacturers to bear the cost of freight on cores, heads, and rods returned.

8. When cores are returned, no allowance to be made for paper remaining on same except that allowance be made for clean white waste at market price for such waste.

9. Customers to be credited with the net weight of cores returned, stripped, at the full selling price of the paper.

10. The average variation in the nominal weight not to exceed four per cent. (4 per cent.) above or below the ordered weight, paper within this range to constitute a good delivery.

11. Paper to be billed at the ordered weight, and no allowance to be made by manufacturer unless variation is in excess of four per cent. (4 per cent.).

12. No paper to be made one weight and stencilled another.

13. Paper must be marked by the manufacturer the ream weight ordered, and there shall be no evasion by substituting letters or symbols for figures.

14. The base selling price to be for paper put up in rolls without heads and rods, and sheet paper put up in bundles soft fold.

15. For paper finished in any manner except as specified in Article 14, additional cost thereof to be added, estimated as follows :—

If finished flat in skeleton frames, not less than 10 cents per 100 pounds to be added to the base selling price.

If finished in solid board frames top and bottom, or in cases, not less than 20 cents per 100 pounds to be added to the base selling price.

16. Case linings to be charged at the selling price of the paper.

17. For trimming sheets on one or two sides, the cost thereof, estimated at not less than 10 cents per 100 pounds, to be added to the base selling price; and for trimming on three or four sides, the cost thereof, estimated at not less than 20 cents per 100 pounds, to be added to the base selling price.

18. For ream wrapping, the cost thereof, estimated at not less than 10 cents per 100 pounds, to be added to the base selling price.

[THE END]

INDEX.

ABERDEEN: THE UNIVERSITY PRESS

THE TREATMENT OF PAPER

FOR SPECIAL PURPOSES

A PRACTICAL INTRODUCTION TO THE PREPARATION OF PAPER PRODUCTS FOR A GREAT VARIETY OF PURPOSES

SUCH AS

Parchment Paper, Transfer Papers, Preservative Papers, Grained Transfer Papers, Fireproof and Antifalsification Papers, Polishing Papers, Tracing and Copying Papers, Chalk and Litho Transfer Papers, Leather Papers, Luminous Papers, Tortoiseshell and Ivory Papers, Metal Papers, Coloured Papers, etc., etc., and Paper Articles.

TRANSLATED FROM THE GERMAN OF

LOUIS EDGAR ANDÉS

CROWN 8VO 250 PAGES 48 ILLUSTRATIONS

PRICE 7s. NET (POST FREE, 7s. 6d. HOME; 7s. 8d. ABROAD)

PUBLISHED BY
SCOTT, GREENWOOD & SON
8 BROADWAY, LUDGATE, LONDON, E.C. 4
(318)

THE ART OF LITHOGRAPHY

A COMPLETE PRACTICAL MANUAL
OF PLANOGRAPHIC PRINTING

BY

H. J. RHODES

DEMY 8VO 344 PAGES 120 ILLUSTRATIONS
2 FOLDING PLATES AND COPIOUS COMBINED INDEX AND GLOSSARY

CONTENTS

Chapter I. The Basis of Lithography.
Chapter II. Lithographic Stones.
Chapter III. Aluminium and Zinc Plates.
Chapter IV. Chemicals and other Materials used in Lithography.
Chapter V. Drawing, Proving, and Hand-press Work.
Chapter VI. Transfer Papers and Inks.
Chapter VII. Transfers.
Chapter VIII. Patching or Imposition of the Transfers.
Chapter IX. Hand and Power Transferring and Printing Presses.
Chapter X. Transferring.
Chapter XI. A Simple, Labour-saving Transferring Process.
Chapter XII. Reducing and Enlarging by Machine Process.
Chapter XIII. Transposing and Reversing.
Chapter XIV. Paper.
Chapter XV. The Theory of Colour.
Chapter XVI. Printing Inks.
Chapter XVII. Lithographic Printing Machines. Direct Flat-bed Machines.
Chapter XVIII. Machine and Hand-press Rollers.
Chapter XIX. Rotary and Offset Machines—Introductory—The Direct Rotary Machine—The Flat-bed Offset Machine—The Rotary Offset Machine—Automatic Accessories of Lithographic Machines.
Chapter XX. Examples of Printing Machines.
Chapter XXI. Machine Management.
Chapter XXII. Machine Printing from Stone.
Chapter XXIII. Printing Chromo or Colour Work.
Chapter XXIV. Machine Printing from Metal Plates—Flat-bed Printing—Rotary Printing.
Chapter XXV. Special Finishing and Other Processes.
Chapter XXVI. Direct Photo-lithography in Line and Half-tone.
Chapter XXVII. Litho Printing on Fabrics and Tinplate: Decalcomanie Transfers.
Chapter XXVIII. Collotype Printing.
Chapter XXIX. Copperplate or Intaglio Printing.
Chapter XXX. Estimating and Costing.
Chapter XXXI. The Training of Apprentices.
Copious Combined Index and Glossary.

PRICE 12s. 6d. NET (POST FREE, 13s. HOME; 13s. 4d. ABROAD)

PUBLISHED BY

SCOTT, GREENWOOD & SON
8 BROADWAY, LUDGATE, LONDON, E.C. 4

THE PRINTERS' AND STATIONERS'

READY RECKONER
AND COMPENDIUM

BY

VICTOR GRAHAM

CONTENTS

Price per Sheet and per Quire, rising by 3 Sheets, from 5s. to 20s. per Ream (rising by 6d. per Ream)—Price per Ream, from 1 to 50 Reams, at from 5s. to 20s. per Ream—Price per lb. (1 lb. to 28 lb.), and 1 qr., 2 qrs., and 3 qrs., at from 5s. to 20s.—Cost of 100, 250, 750, and 1,000 Sheets of Folio, 3to, 4to, 8vo, 12mo, 16mo, and 32mo, at from 5s. to 20s. per Ream—Fractional Parts of 5s. to 20s. (rising by 6d.)—Dozens and Grosses, from 5s. to 20s. (rising by 6d.)—Useful Multiples, of from 5s. to 20s.—Cost of Quires at price per Ream, from 2d. per Quire to 2s. per Quire (rising by ¼d. per Quire up to 1s.; and then by ½d. per Quire)—Price per lb. to price per Ream—Cost of Cards per 1,000 (3rds, Extra 3rds, Small, Large, Double Small, Double Large), at from 5s. to 30s. out of Royal—Quantity Table (showing Paper required to Print 1,000 Copies of a Book in any form from 8vo to 32mo)—Table for giving Out Paper from Folio to 48mo, 50 to 20,000—Sizes and Weights of Paper—Sub-divisions of Paper—Equivalent Weights of Paper—Sizes of Millboards—Sizes of Cardboard and Bristol Boards—Sizes of Cut Cards—Waste Cards—Cards Out of Royal—Strawboards and Woodpulp Boards—Sizes of Account Books—Sizes of Portfolios — Notes on Account Books — Index for Account Books — Patterns of Account Book Rulings—Sizes of Tea and Tobacco Papers—Number of Pages in Given Number of Quires—Printing Monthly Calendars—Forms of Bills, etc.—Table of Discounts or Interest—Practice Tables—Holidays and Quarter-Days—Average Number of Ems to a Foot—Sizes of Point Bodies and Old British Bodies—Sizes of Spaces—Leads to a lb.—Sizes of Wood Furniture—Justifying with Leads — Measure for Bookwork — Difference between Type Bodies — London Compositors' Bookwork Scale—Sizes of Platens of Presses—Sizes of Envelopes, and How best to cut out—Weights and Measures in Improved Form — Dictionary of Useful Words — Correcting Proofs — Book-keeping specially adapted for Printers.

CROWN 8VO 112 PAGES

PRICE 4s. 6d. NET (POST FREE, 4s. 11d. HOME; 5s. ABROAD)

PUBLISHED BY

SCOTT, GREENWOOD & SON

8 BROADWAY, LUDGATE, LONDON, E.C. 4

(320)

Stevens, Henry Potter
The paper mill chemist
2d rev. and enl. ed.