WOOD · PULP
AND · ITS · USES

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R · W · SINDALL

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WOOD PULP AND ITS USES

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BY

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WITH THE COLLABORATION OF

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PREFACE

The world has had its Stone age and its Bronze age: later its Iron age, and the present is a Cellulose age.

This is not said *ad captandum:* it is a statement which will survive critical examination.

The volume now offered to students and the general public is based on studies in the domain of cellulose, both theoretical and scientific, and practical or industrial.

It is not a monograph or a text-book of the subject: it does not pretend to be systematic or exhaustive.

Technical literature in these days threatens to develop to formidable dimensions; and systematic works on branches of technology necessarily carry a large weight of fact and information which is common groundwork.

We have only given an outline of what appears essential as a cyclopædic framework. We are not addressing ourselves particularly to the specialist, nor to the technical student. Rather to the general reader, and our aim is therefore to give a general account of the evolution of the wood pulp industries, as typical of the age we live in, and as a very substantial contribution to its primary necessities.

But if wood pulp has had an interesting past history, its future is suggestive of many more interesting possibilities of which we endeavour to give indications.

From whatever standpoint in fact the subject is treated, it challenges attention.

The chemist, the manufacturer, the political economist, and of course the financier will find that it teems with problems the solution of which carries rewards of great moment.

In an age when pessimists see little but competitive exhaustion of sources of natural wealth, it is satisfactory to be able to present a domain still full of unexplored possibilities. Such is the subject of "wood pulp" or, more broadly, "cellulose," and we trust this imperfect contribution will help to sustain and awaken the interest of readers and students.

We have pleasure in acknowledging the valuable assistance of Mr. W. N. Bacon B.Sc., F.I.C., in contributing matter and revising proofs.

We are indebted to the Royal Society for the privilege of reproducing illustrations from papers of the late W. J. Russell (p. 73). To Messrs. Longmans, for permission to reproduce portions of "Researches on Cellulose," II.

The illustrations in Chapter I. are chiefly from original histological studies of Messrs. Flatters, Milborne and McKechine (Longsight, Manchester), whose excellent work in this field is well known, or should be, to all students of Botany.

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WOOD PULP AND ITS USES

CHAPTER I

THE STRUCTURAL ELEMENTS OF WOOD

There are no more interesting studies than those which group themselves under the term Applied Sciences. It is quite true that science, or rather the sciences, may be pursued from a point of view which ignores the services which they render to man; but whereas "pure science" is an ideal rather of the imaginative world, the natural prosecution of the sciences compels the recognition of their organic interdependence with human progress.

Whichever aspect is the more attractive on general grounds, it is clear that the subject of this work is prominently typical of this interdependence; involves in a particular manner the utilitarian bearings of science, and our treatment of it must be accordingly utilitarian.

Wood pulp is a comparatively modern product called into existence as a paper maker's raw material. The woods which furnish the product in its various forms have been impressed into the service of man from the earliest, in fact from prehistoric, times, and have been used for their structural qualities in a large number of our most important industries. The uses of the woods are so universally familiar that it would be superfluous to particularise them.

We may, however, preface our specialisation to the particular employment of certain woods as the basis of wood pulp, by calling attention to the physical and mechanical properties of a typical range of woods considered as structural materials.

For the natural history of the woods as products of vegetable life and growth we turn, of course, in the first instance to the science of Botany. In the scientific treatment of plant life questions of utility—that is, the part which a plant or any of its parts, seed, flower, stem or root, may play in the service of man—has no part. Moreover, external features are of quite subordinate moment.

Thus the cereals which furnish, perhaps, the most important staple of our food are to the botanist no more important than any other of the great family of the grasses. It is not without significance to the botanist that these particular grasses have come to be selected and specialised by cultivation through countless generations, so as to differentiate them as economic products. But such considerations are relatively unimportant, as not concerned in those elements of identity and characterisation which fix the position of an individual plant in the scheme of botanical science.

So also in regard to external features such as size, form, and vegetative habit. The sugar cane or bamboo are not obviously related to the cereals, but to the botanist the relationship is of the closest. The laburnum and the trefoil have little in common as regards form and life history, but they are blood relations.

The relationships are fixed by the more fundamental features of the reproductive mechanism; both the major and minor differentiations constituting the basis of the classifications of botanical science are those of the reproductive system. These differences necessarily are correlated with those of the plant body, by which the second great function or group of functions is conditioned, viz., those of nutrition. As the reproductive mechanism becomes more complex, so the structural type is differentiated towards complexity. Viewing the plant world as an evolutionary series, reproduction by seeds is the last feature to make its appearance, and is preceded by those differentiations of the plant body which issues in what is known as a vascular system.

Thus in the fern the structural features of the higher flowering and seed-bearing plants are recognised, and in a tree fern the differentiation into vascular tissue, leaves and stems, with the lower portion formed into a root system, are apparent. But the reproduction of the fern is on a much lower plane, and it bears no seeds. The tree fern is a kind of pseudo-morph of the true tree or forest tree, which is a spermatophyte or seed-bearing plant.

Of the four great groups of modern botanical classification the spermatophytes are much the most conspicuous and widely distributed. Moreover, they are so interwoven with our experience that their study has often ranked as co-extensive with botanical science to the exclusion of the other great groups. These are the algæ, the lichens, and the fungi (Thallophytes), the mosses (Bryophytes), and ferns, horsetails, and club mosses (Pteridophytes). The modern science regards these groups as related in evolutionary sequence. There are two aspects of this evolution. The one involves the theory of descent, the higher from the lower order, as an objective fact; on the other the development of the highest type can be followed through the lower by the study of the dominant or reproductive functions, which thus unfolds itself as a homogeneous conception of the relations of the infinitely diversified forms of plant life.

We are not concerned with these fundamental generalisations further than to indicate their connection with our subject.

We shall have to point out that from the point of view of "wood pulp" the trees which furnish these industrial products are of two sub-groups, and we have explained the basis of classification sufficiently to convey their relationship to the general reader in the terms employed by the botanist:—

Spermatophytes
(seed-bearing plants)

Gymnosperms
(naked or exposed seeds)
(Coniferæ)
Pine Spruce

Angiosperms
(enclosed seeds)
Monocotyledons
Bamboo
Sugar Cane.
Dicotyledons
Poplar

We have already indicated that our subject has only an incidental connection with these fundamental relations. The plant is a structure, an agglomerate of structural elements; and its work as a plant is to grow, to build up tissue The assimilating organs of the higher flowering plants are the leaves. The leaf is the centre of the fundamental operation of building up "organic" compounds

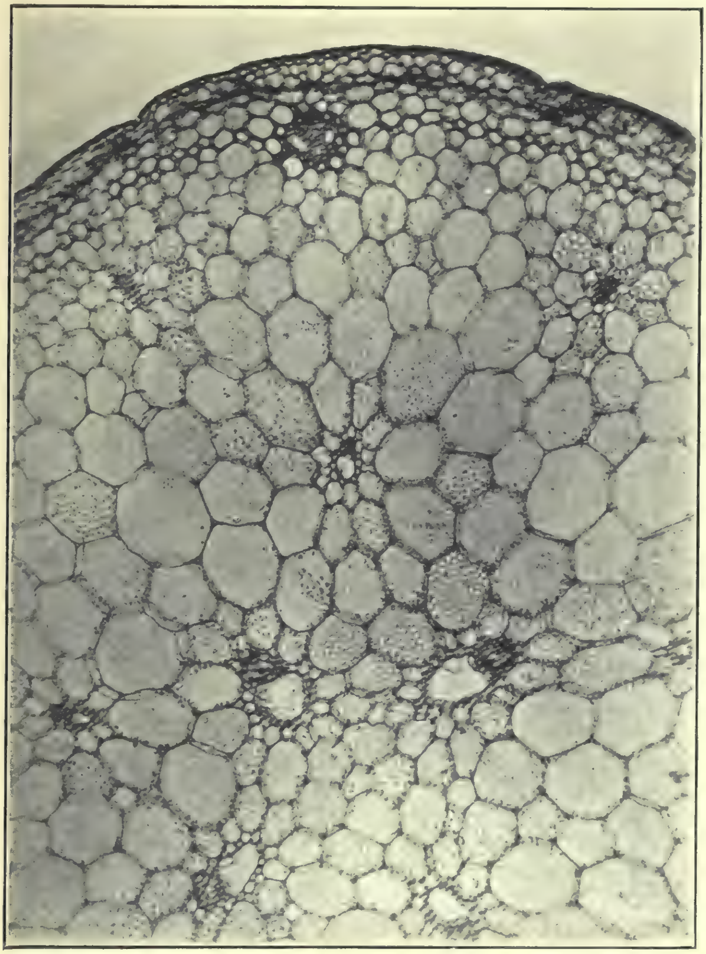


FIG. 1.—Transverse section of stem of Tradescantia showing epidermal tissue, parenchyma containing starch, at the centre a vascular bundle.

from the inorganic form of carbon, viz., carbonic anhydride, contained in the air, and of which gaseous mixture it is a normal constituent. This characteristic function of the plant, the photosynthesis of carbon compounds and their elaboration to tissue material, we must take for granted; as well as the complementary function of the root system

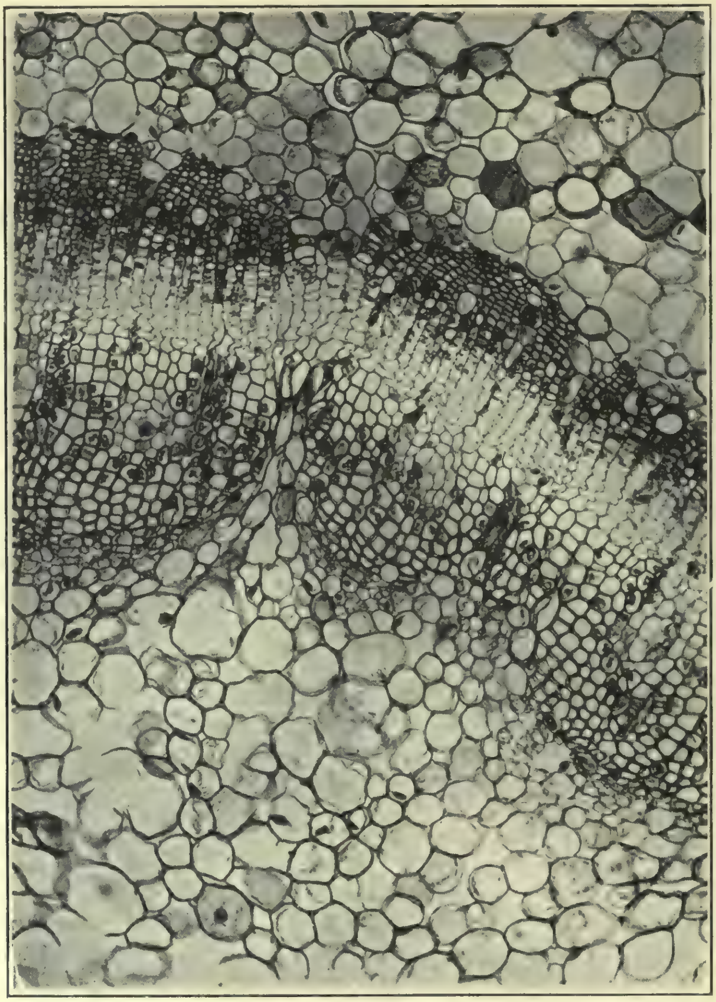


FIG. 2.—Transverse section of a young stem of Pinus Sylvestris (common pine). Below, primary ground tissue followed by wood in development and in succession cambium bast and cortex. In the centre is a medullary ray.

in absorbing water, inorganic mineral compounds, and other nutrient material from the soil.

FIG. 2B.—Transverse section of an older stem of Pinus Sylvestris (common pine) showing developing branch, a more advanced wood system and external to the latter the cambium and phloem tissues.

We are concerned with the plant as a completed structure. The study of those functions and processes from which the structure results, and with which it is in its several parts associated, constitutes the branch of the science known as vegetable physiology; and students who desire a more comprehensive survey of the subject-matter are referred to the special text-books.

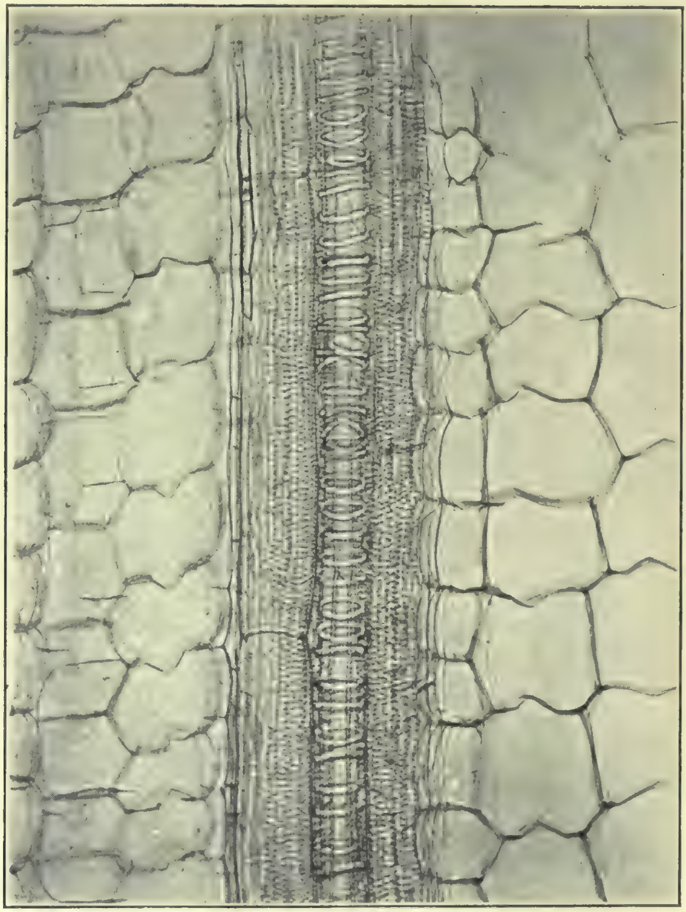


Fig. 3.—Longitudinal section vascular bundle of Zea Mais showing spiral, annular, and pitted vessels. Surrounding the bundle is the ground tissue or parenchyma.

Taking the plant as a structure, we find it an assemblage of units generally known as cells. The typical cell is a spherical body of small dimensions—0·1 and 0·5 mm.

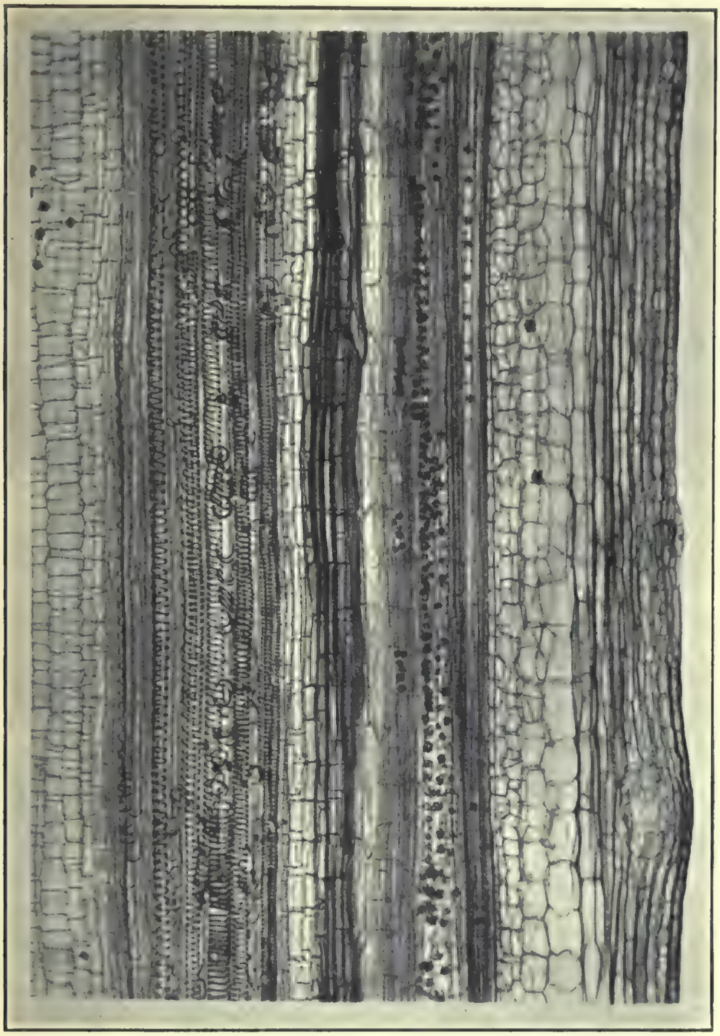


FIG. 4.—Longitudinal section of stem of Gossypium S.P. (cotton plant) showing from left to right pith, spiral vessels, cambium, phloem, cortical tissue, and cuticle.

diameter—and consisting of an enveloping wall enclosing the cell contents.

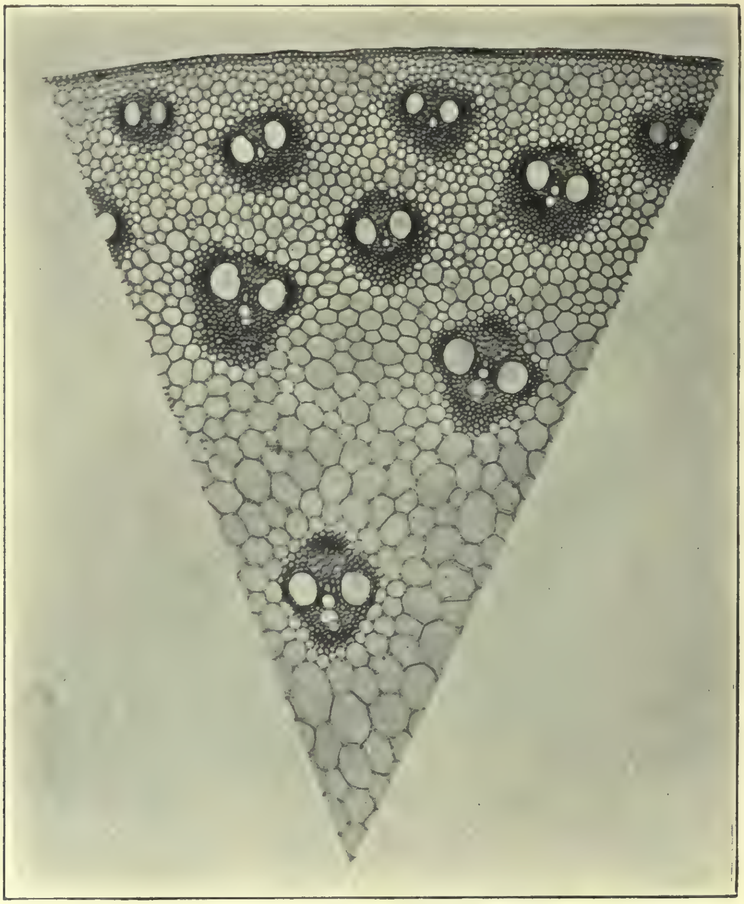
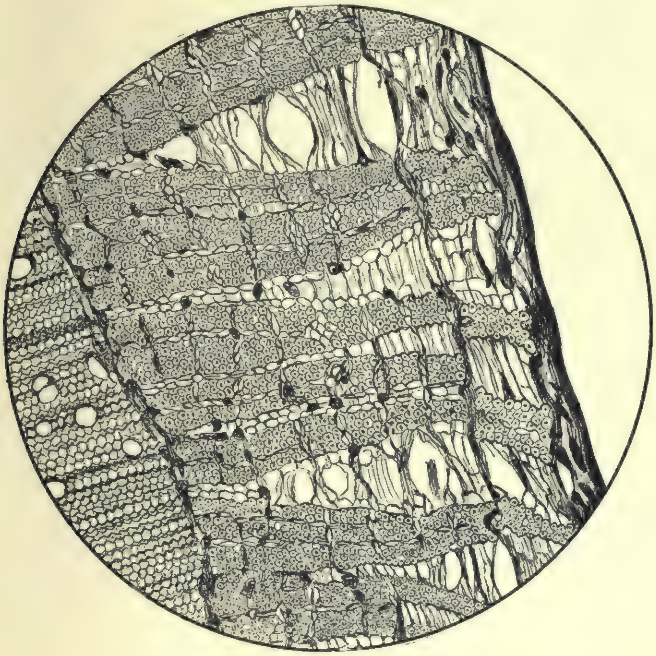


FIG. 5.—Transverse section of stem of Zea Mais (Indian corn). Vascular bundles surrounded by primary ground tissue. Each bundle contains large pitted and annular vessels with phloem and sclerenchyma.

Variations and differentiations of the typical form correspond with infinite diversity of functions and conditions. Typical forms of cellular tissue are represented in Figs. 1—2.

More extreme variations lead to the structural forms classed as fibres and vessels.

These are elongated cells, the length being a very large multiple of the diameter. In a general way "fibres" may be regarded as the strengthening elements of plant structures, and are of relatively simple form. "Vessels" are the seat of complex vital functions and operations involved in nutrition, and are much more diversified in form. Typical fibres and vessels are represented in Figs. 3—4.



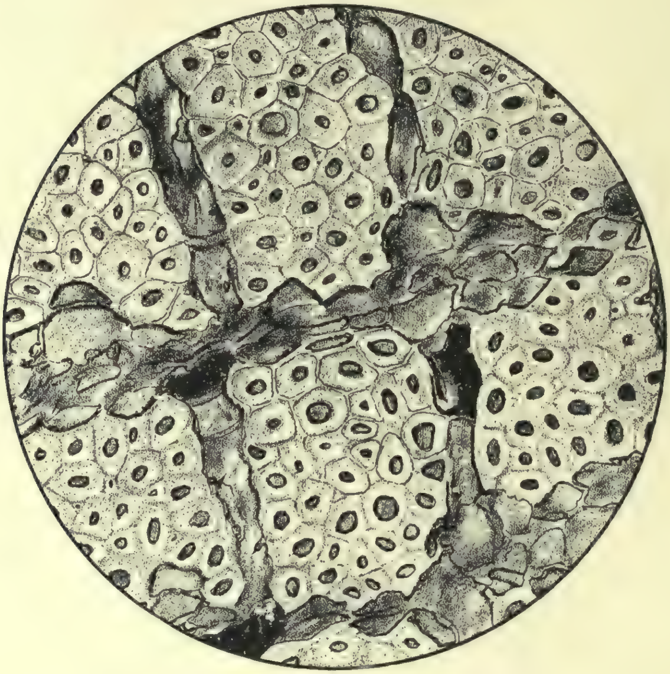
Jute.

Fig. 5b.—Section of bast region showing wedge-shaped bundles extending from cambium to cortex.

The arrangement of cells, fibres, and vessels in the stem of a plant is co-ordinated with those characteristics which determine its position in the evolutionary series. We may briefly describe stems which are typical of the two main divisions of the highest group of flowering plants.

Fig. 5 represents a section of the stem of a monocotyledon.

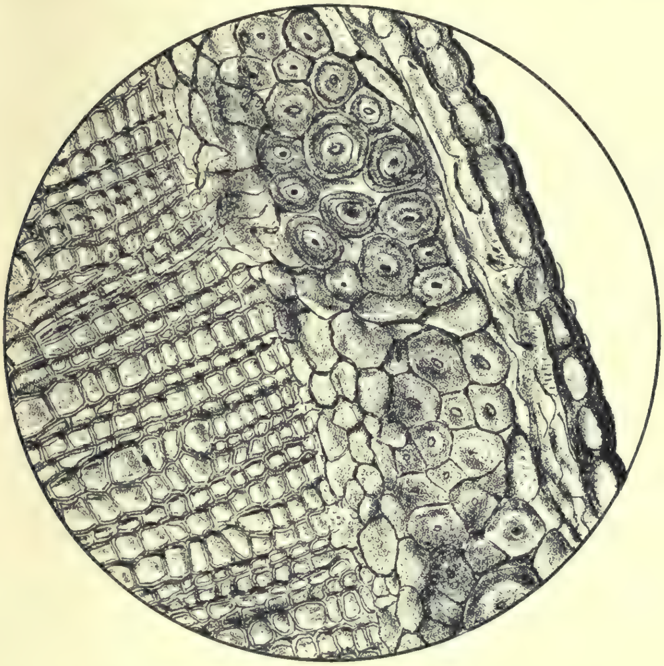
These structural types introduce the fundamental considerations involved in differentiation of tissues; ground tissue, known as parenchyma, is made up of thin naked cells showing equality in their dimensions, though occasionally elongated. The earliest differentiation of the ground tissue separates nutritive cells from reproductive cells: in the building up of the plant body we are concerned with the former only, and their further specialisation



Jute (mag. 300).

Fig. 5c.—Section of bast region showing structure of bundles and thickening of ultimate fibres.

is an adaptation to mechanical and physical exigencies rather than for vital purposes. The requirements to be met are (1) for the transportation of nutritive matter from the leaves where it is manufactured, as well as of water absorbed by the roots. Hence the provision of conducting tissue—or mestome; (2) the plant, to maintain its form, requires mechanical support, and tissue is differentiated into rigid structures known as stereome.



Flax.

Fig. 5d.—Section of stem of Linum showing groups of bast fibres lying between wood and cortex.

These features are generally illustrated in the annexed figure, showing in section the stems of two dicotyledonous annuals, flax and jute, and of a monocotyledonous annual Indian corn (Zea Mais).

They will be better understood after dealing with the more complex case of the perennial stem. The formation of wood, *i.e.*, massive wood, is a process which is concerned with the growth of trees, and although the perennial growth introduces no new structural elements, it does present a certain development of plan or arrangement beyond that of the annual stem. At the outset we notice there is a contrast of the dicotyl (or conifer) stem with the monocotyl, and since the supply of wood pulp is at this date exclusively drawn from wood of the former types, we must set out their typical characteristics in some detail.

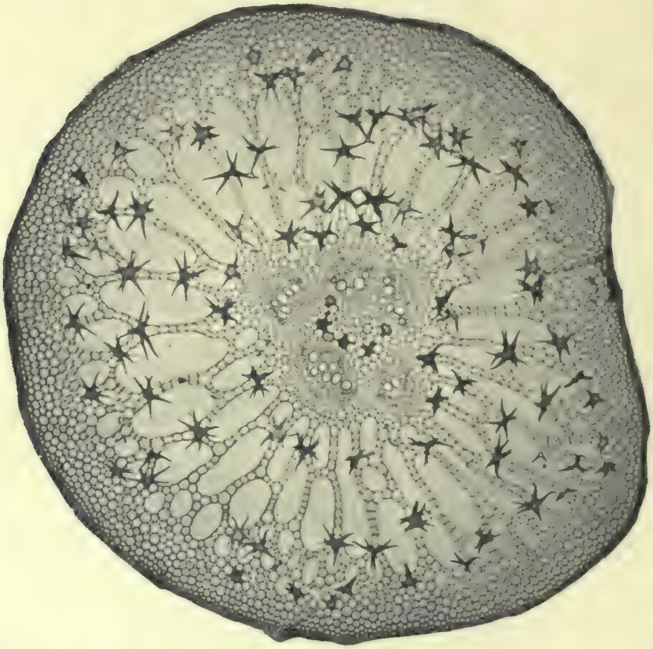


FIG. 6.—Transverse section of stem of Lymnanthemum (aquatic plant). Central axis with xylem and phloem elements. Ground tissue showing large air cells producing buoyancy, and star-shaped idioblasts.

The apex of a growing stem exhibits an active condition of cell division with a differentiation into definite regions, which becomes more marked as we proceed downwards. In the finally differentiated stem these are marked out as (a) epidermis, the external protective tissue; (b) the central cylinder, or stele, and between them (c) the cortex. (Lymnanthemum, Fig. 6.)

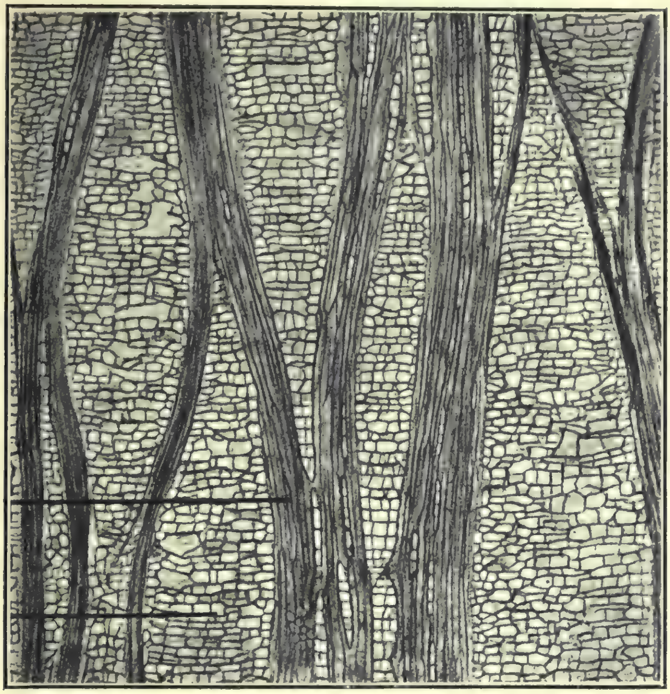


Fig. 7.—Transverse longitudinal section of stem of Tilia Europœa (Lime Tree), showing bast fibres and ground tissue.

In the perennial stem the epidermis does not keep pace with the increasing diameter, and the cortex becomes the external protective tissue known as cork, with its well-known impervious characteristics. The cortex is complex in structure.

It contains active chlorophyllic and assimilating tissue, and cells which have a storage function ; also well-marked storage tissues known as collenchyma, or sheathing tissue, and sclerenchyma, or hard tissue. The latter is, from the

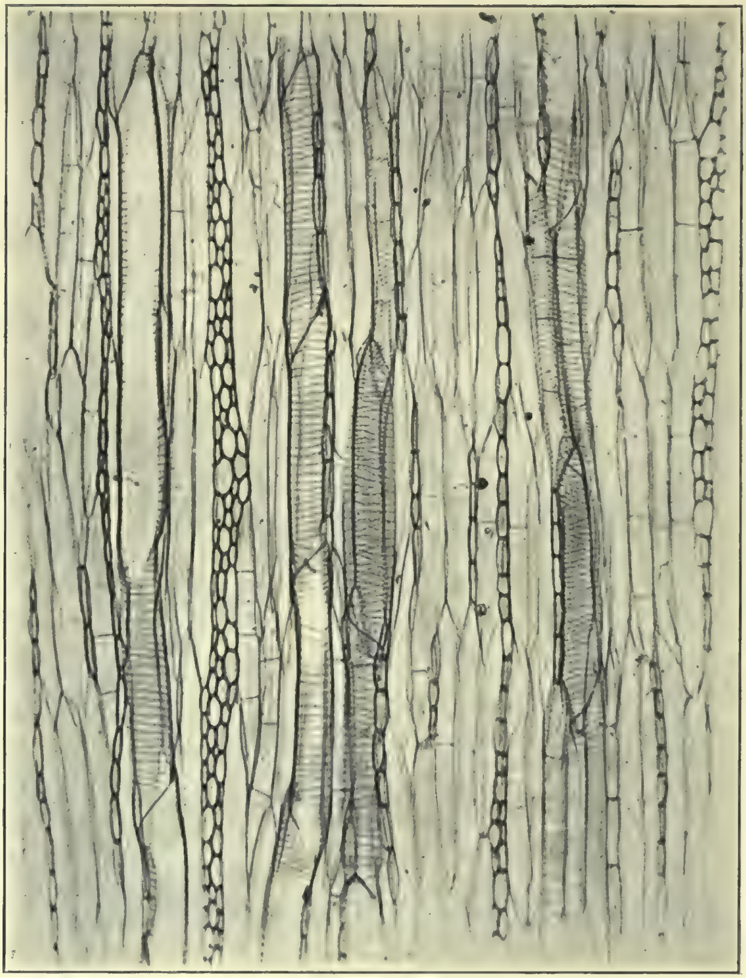


FIG. 8.—Tangential longitudinal section through the wood elements of Tilia Europœa (Lime tree). From left to right a medullary ray is seen in the row of little cells, followed by typical wood fibres, spiral and pitted vessels, and connective tissue.

present point of view, the more important, as it includes the elongated thick-walled cells known as fibres (Fig. 8). In the central cylinder, or stele, the vascular tissue is prominent (Fig. 7). There are two well-marked types of vessels—the tracheæ, which are of large diameter, with heavy walls variously modified in structure into spiral bands, rings, or reticulations (Fig. 8).

FIG. 9.—Longitudinal radial section of Pinus Sylvestris timber showing well-developed bordered pits upon the walls of the tracheids. At right angles to the tracheids is a medullary ray.

Being destined for water conduction, they are arranged end to end in a continuous longitudinal series. In the conifer stem there is very large characteristic development of the tracheal-like tissue; but the constituent vessels differ from the true tracheæ in having tapering ends, and in not being disposed in longitudinal series.

These vessels are called tracheids, and they are characterised by pitted walls which, under the microscope, appear as double concentric rings arranged in rows (Figs. 9 and 10). The second type of vessel is the sieve tube, so called from the specially perforated area which they develop, termed the callus plate. They are concerned in the conduction and distribution of organic nutrient matter.

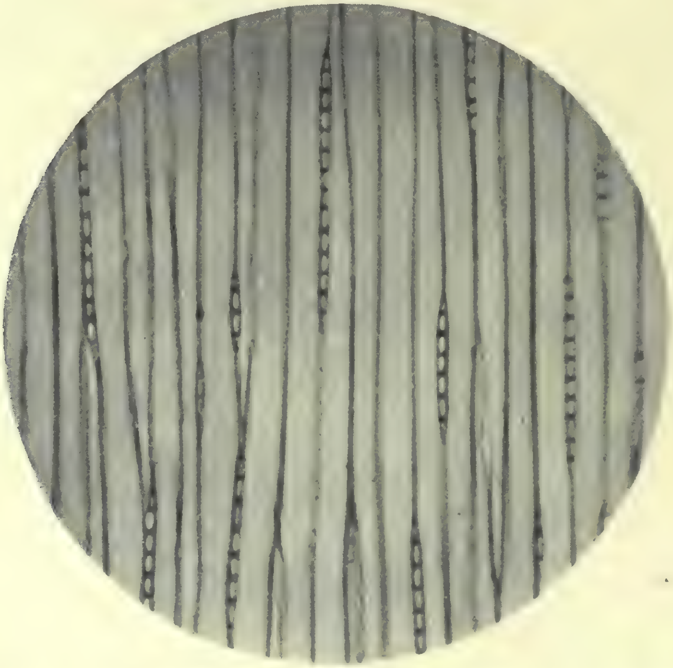


FIG. 10.—Tangential longitudinal section of old wood of Pinus showing tracheids and medullary rays; the latter consist of two or more rows of cells arranged longitudinally.

These two types of vessels are characteristic respectively of the xylem or wood, and phloem or bast. In the dicotyledonous stem the strands of xylem and phloem, though separate, are organised together into vascular bundles. The disposition and relation of these bundles are the characteristic of the exogenous stem.

They form a centric system—the xylem towards the centre, the phloem towards the periphery. The parenchyma enclosed in the vascular cylinder is the pith or medulla, and its extensions outwards between the vascular bundles are called pith or medullary rays, and act as storage cells for reserve food material.

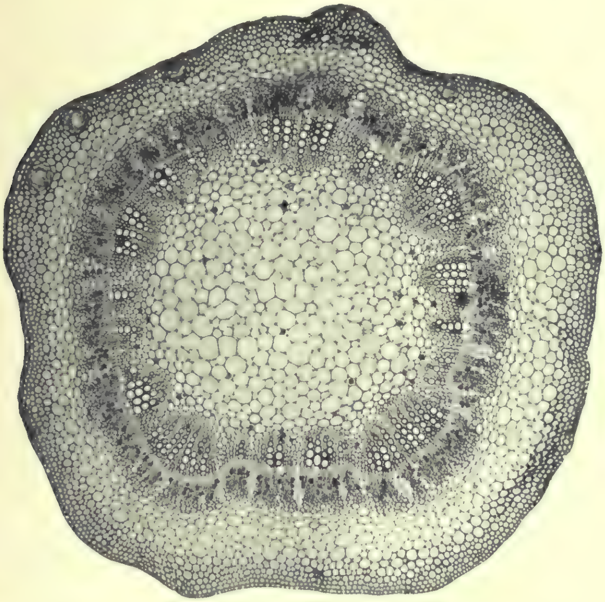


FIG. 11A.—Transverse section of stem of Gossypium (cotton plant) showing one annular ring of xylem and phloem elements with intervening cambium layer.

But the most obvious feature of the transverse section of a forest tree, viz., the annual rings, remains to be elucidated.

In the xylem-phloem bundles there is a central portion of meristematic tissue, which continues the process of cell division and differentiation, contributing new xylem on the one side and phloem on the other. And further, this active tissue, known as cambium, extends from bundle to bundle across the pith (rays), assuming therefore a structural ring. The annual accretion of new tissue, which is a product of the cambium, is thus marked as in a ring. (Fig. 11A.)

As the trunk or stem increases in girth, an increasing portion of the xylem ceases to take part in the conduction of water, the ascending sap passes through the younger tissues or sap wood, which becomes differentiated in colour and other aspects from the heart wood; in fact, it is this differentiation of the sap wood from the heart wood by the formation of vessels, tracheids, and fibres of larger diameter and thinner walls in the former tissues, that serves to accentuate the well-marked characters of the rings. (Fig. 11B.) The concentricity of the rings varies also in different trees; the gymnosperms, for example, are extremely regular, whilst in some angiosperms the rings are more or less wavy, and in others again, such as the beech, the rings are crested. The new phloem deposited in contact with the old, causes rupture of the latter, and it pulls or scales away more or less rapidly.

The bark of trees is very complex in structure, very variable in character both as regards its structural components and its proportion and massive distribution; generally it is not permanently associated with the stem or trunk, as are the new wood tissues. This is also in accordance with our superficial observations of the habits of trees.

The conspicuous feature of the dicotyledonous stem is, therefore, the collateral vascular bundle, open in the sense that the cambium constitutes a connecting tissue linking the bundles. In contrast with this, the monocotyledonous stem is composed essentially of a ground tissue, and

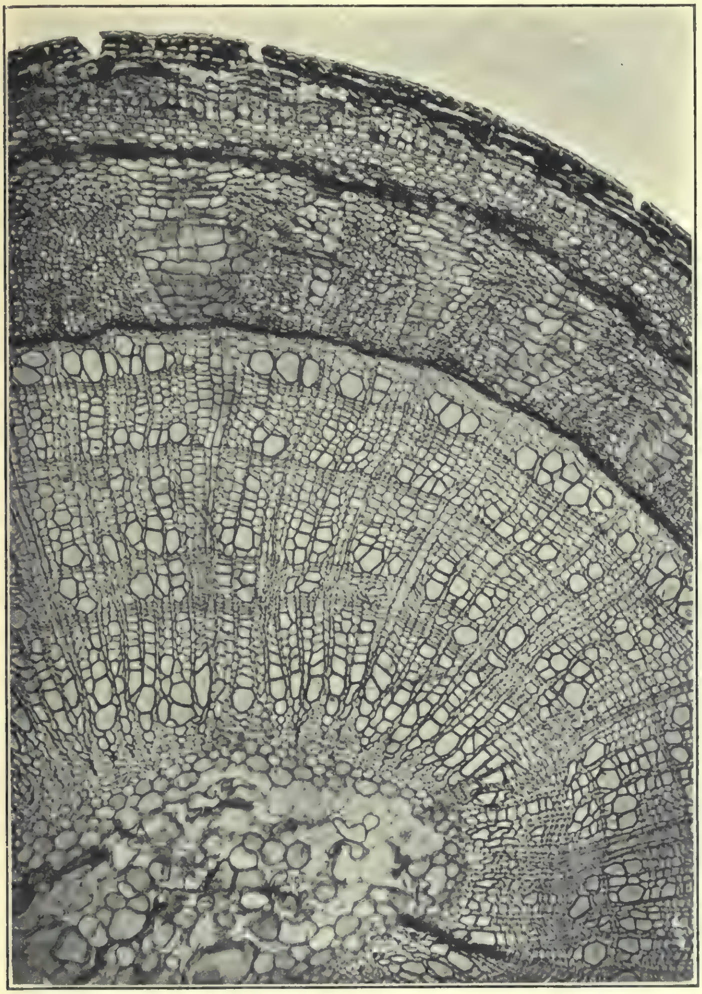


FIG. 11B.—Transverse section of a three-year-old stem of Tilia (Lime Tree). At centre pith then xylem (wood) in three separate rings. Towards the periphery the cambium ring then phloem and cortical tissue.

scattered but closed fibro-vascular bundles, *i.e.*, with no connecting cambium (see Fig. 5).

This arrangement implies an absence of provision for large increase of diameter, and the stem of a perennial of this type is columnar or cylindrical rather than conical.

There is a corresponding lack of provision for developing an increase of foliage by way of a system of branches. The foliage is thus a crown of leaves, as in the palm (Fig. 12), which remains very much the same from year to year. (Compare with Figs. 12B, 12C.) The vascular bundles generally develop stereome tissue, *i.e.*, sclerenchymatous thick-walled fibres which, in association with the vessels, constitute the fibres and vascular bundles.

FIG. 12.—Date Palm. Typical Monocotyledon Perennial.

We have now become aware of the principal structural elements of a wooded stem, and we can analyse some of the aspects of wood sections which are familiar to us as the "grain."

Usually the xylem elements are parallel to the axis, in which case we have the term "straight grain"; but irregularities appear in the growth of the various tissues

FIG. 12B.—Pine. Typical Conifer. Exogenous Gymnosperm.

(1) by a continuation of the growth of the cells after separation from the cambium proper, thus causing an interlacing of the fibrous elements, with a consequent cross-grain

effect; or (2) in the formation of branches and adventitious buds, producing the effect known as "burr." Other irregularities are seen in the projections of the xylem elements from the rings, causing the "bird's-eye" effect so well marked in the maple.

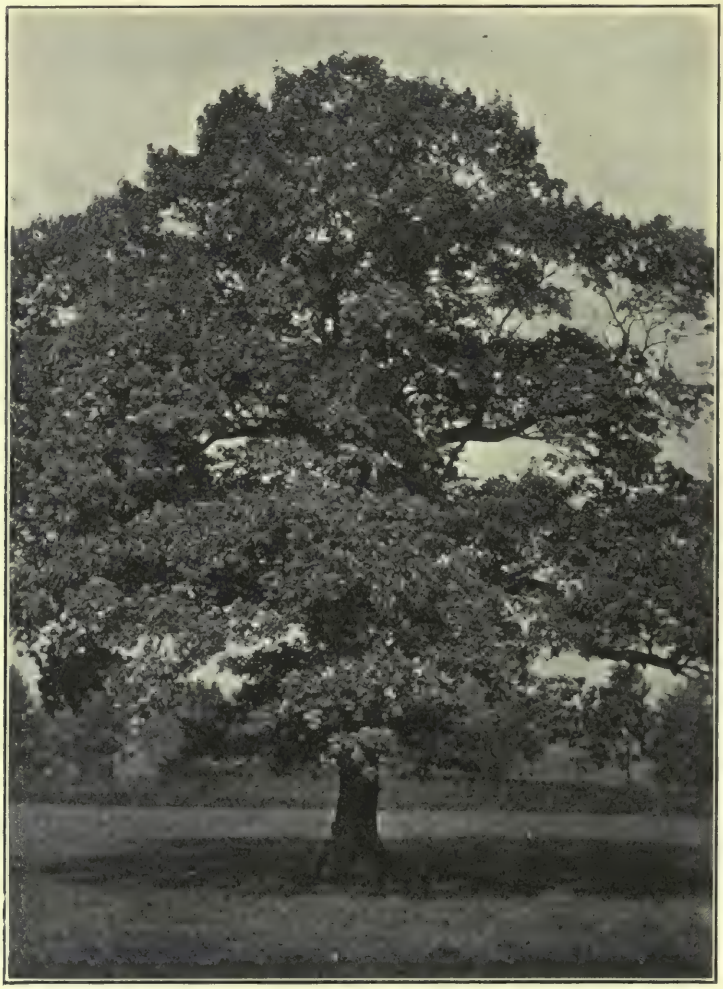


FIG. 12C.—Oak. Typical Angiosperm Exogenous Perennial.

In the angiosperms the medullary rays are much more highly developed than in the gymnosperms, and constitute in some cases a large percentage of the wood.

In the oak the primary medullary rays may be built up of several hundred rows of cells, and when seen in radial sections appear as silvery bands, or silver grain, as it is termed.

Some of the poplars frequently have the medullary system aggregated together in spots known as "pith flecks," which help to identify the species.

We may note that in addition to the formation of the ligno-cellulose or primary plant substance (see p. 57), various other products of secretion are formed. Proteins, or nitrogenous bodies, carbohydrates, glucosides, resins, and other aromatic substances, acids, such as tannic acid, dye stuffs, which impart particular characters to the woods, and aid in its identification.

Physical Properties of Woods.

Weight.—This depends upon the condition of the wood in relation to moisture, and as regards structure, *i.e.*, upon the proportion of small heavily lignified vessels such as would be illustrated by the "heart wood," this being relatively much more dense than the more distended vessels of the "sap wood."

The following table illustrates the density of various woods:—

	Wood.	Density.	
Very light	Poplar	0·26	0·4
Light	Spruce and Pine	0·4	0·6
Moderately heavy	Birch and Beech	0·6	0·7
Heavy	Oak	0·8 and upwards	

Hardness.—This is usually measured in terms of the number of kilograms required to force a punch of 1 sq. cm. in area to a depth of 1·27 mm. into the wood, perpendicular to the direction of the fibres.

The following table illustrates the relative hardness in decreasing proportions :—

Wood.	Hardness in kilograms per sq. cm.
Lignum Vitæ	793
Oak	225
Beech	200
Most coniferous woods	100
Cotton tree *Bombax Malabaricum* (type of softest wood)	—

Strength of Woods.—This may be defined as the resistance offered by the wood to any force tending to break the fibres across (transverse stress), or to overcome the cohesion of the fibres (longitudinal stress).

In the testing of woods various other stresses are applied; but the breaking strain, as stated above, is by far the most important.

It is found that in broad-leaved trees the lateral resistance is from $\frac{1}{6}$th to $\frac{1}{4}$th of the longitudinal resistance, and in the coniferous $\frac{1}{20}$th to $\frac{1}{10}$th.

Tetmayer of Zurich has arranged in the following table the relative resistance of the woods to various stresses :—

Transverse Pressure.	Tension.	Crushing.	Shearing.
Beech	Beech	Oak	Beech
Oak	Oak	Beech	Oak.

Transverse Pressure.	Tension.	Crushing.	Shearing.
Larch	Scotch Pine	Larch	Larch
Silver Fir	Larch	Silver Fir	Spruce
Spruce	Spruce	Spruce	Silver Fir
Scotch Pine	Silver Fir	Scotch Pine	Scotch Pine.

It was found that Scotch pine had the lowest technical value, silver fir 20 per cent. greater, spruce 26 per cent. greater, larch 66 per cent. greater, oak beech 95 per cent. greater.

Two other factors usually determined in wood are (1) the ash, that is the amount of inorganic constituents left after burning the wood, which is a small proportion by weight though voluminous ; (2) the calorific, or fuel, value of the wood. On an average it is found to be about 4,000 calories or heat units, in other words, one unit of weight of dry wood on burning furnishes heat which would raise 4,000 units of weight of water 1° C.

The foregoing brief *exposé* implies the fundamental conditions of fitness of a given wood or wood substance for conversion into a fibrous raw material. These are primarily a large proportion of elongated cells or fibre, and, as the basis of economic production of such pulps, it will be obvious that the massive perennial stem fulfils essential industrial conditions of growth, transport, and treatment for conversion into pulp, which result in low cost of production.

The processes of pulping to be dealt with in a subsequent chapter, are of two kinds : (1) a simple disintegration by wet-grinding, to a " mechanical " pulp. Such pulps are substantially the original wood substance, deprived incidentally of water-soluble constituents (see p. 97); (2) chemical processes which attack the ligneous constituents and convert them into soluble derivatives, leaving the cellulose which preserves the form and dimensions of the original fibres constituting a "chemical" pulp composed of the fibrous structural elements of the wood in the fully resolved condition (see p. 120).

The number of woods fulfilling what is a very exacting specification of requirements, is extremely limited. Actually the wood pulp industry is based upon the utilisation of coniferous woods and poplar.

CHAPTER II

I. CELLULOSE AS A CHEMICAL INDIVIDUAL AND TYPICAL COLLOID. II. THE LIGNONE COMPLEX, LIGNO-CELLULOSE; SPECIAL CHEMICAL NOTE ON AUTOXIDATION, AND RESEARCHES OF W. J. RUSSELL

THE investigation of the nature and composition of the woods is a problem of "organic chemistry." The wood substance is in all cases a complex of carbon compounds. The woods present variations in composition which are definite and characteristic; but these are only minor divergences from a common type. As representative of the type we may take two individuals.

The jute fibre—the lignified bast fibre of an annual, a simple tissue—and beech-wood, which represents perennial growth, and from its nature is an assemblage or mixture of structural elements.

We have in the previous chapter spoken of "lignification" as a process. Morphologically it is a process of thickening by incrustation, and according to recent researches this incrustation is a process of forming adsorption compounds, the colloidal hydrated celluloses first elaborated, taking up soluble colloidal products from solution in the cambium fluids or "sap" (H. Wislicenus, *Zeitsch. Kolloide*, 1910, p. 17); chemically it is regarded as the formation of a cellulose derivative by combination of cellulose with certain acid and unsaturated ketonic groups, the resulting compound or complex being a *ligno-cellulose*. Conversely, by various processes which attack these acid and unsaturated groups, the ligno-cellulose is resolved into derivatives of the latter which are soluble, and cellulose which is resistant and insoluble. The separation or isolation of cellulose is attended by disintegration; the aggregated structure is resolved into its component units, which are cells, including in this general term fibres and vessels. In the ligno-celluloses these are of small dimensions, 2—3 mm. in length, and ·02—·03 diameter. A mass of such units in contact with water constitutes a "pulp." The separated cells retain their dimensions and general structural characteristics notwithstanding that the elimination of the non-cellulose components is attended by considerable loss of substance, *i.e.*, weight, and the cellulose may therefore be regarded as the more permanent skeleton or framework of the cell. The quantitative relations of this resolution are of importance. The following percentage numbers characterise the typical ligno-celluloses :—

	Cellulose.	Lignone.
Jute	70—80	30—20
Beechwood	50—60	50—40

It may assist the student in estimating the practical significance of these chemical facts to point out that a ligno-cellulose is related to cellulose somewhat in the same way as an alloy of gold with baser metals is to gold. Gold as a "noble metal" is relatively non-reactive, and especially distinguished by resistance to oxygen, and is therefore permanent in the air and generally unaffected by the conditions which prevail on the earth's surface. Cellulose is resistant to oxygen and water, and is permanent under the prevailing conditions of our planet. A gold alloy is amenable to the attack of oxygen which combines with the constituent metals, converting them into oxides, or of reagents which dissolve the baser metals as salts: the gold is left as elementary metal. Similarly, cellulose is obtained as a residue resisting the action of reagents such as chlorine, caustic alkalis or bisulphites, all of which combine directly with the lignone groups, for reasons which will appear.

It would take us outside the scope of our present treatment of the subject to attempt an exhaustive *exposé* of the chemistry of these natural products. The special outline which we give may be regarded as the irreducible minimum necessary as the foundation of the chemical technology of the subject. We have already implied that the woods are modified celluloses, from which their more important constituent, that is the cellulose, is readily isolated.

Cellulose is a carbohydrate; it is derived from the sugars and under severe treatment may be resolved into sugars. Its ultimate composition is represented by the formula $n(C_6H_{10}O_5)$, and, in breaking down to the simplest sugar, $C_6H_{12}O_6$ the process may be formulated as one of simple "hydrolysis": $n(C_6H_{10}O_5) + nH_2O = nC_6H_{12}O_6$. But of the mechanism of this resolution we are profoundly ignorant. Indeed, it cannot be said that the above equation of hydrolysis has been verified experimentally. Recent researches of H. Ost and L. Wilkening (*Chem. Zeit.*, 1910, 34, 461), establish a conversion of cellulose into fermentable sugars to the extent of 90 per cent. of its weight, with a residue of acid products. The above equation is therefore not more than an approximate picture of the underlying facts. This is equivalent to the statement that we are entirely ignorant of the actual constitution of cellulose.

We are more familiar with another complex carbohydrate, starch, which has a similar empirical formula $n(C_6H_{10}O_5)$. Starch is quantitatively resolved into the sugars, maltose and dextrose, by hydrolytic action determined by reagents or by ferment actions and under conditions which enable us to follow minutely the stages of the transformation. These reveal the extreme complexity of the aggregate which constitutes starch. But although we can closely follow this chemical disintegration through its stages, we are unable to integrate these results of analysis into a formula, still less by any laboratory process to reascend the scale and transform the products of resolution back to starch. *A fortiori*, the proximate constitution of cellulose is problematical.

Starch and cellulose are not only closely linked by many analogies which have been established by comparative investigation in the laboratory, but in the plant they stand in intimate, in fact genetic, relationship, as evidenced by the transformation from one to another, and the equivalence of their vital functions in many respects. Premising these relationships, we may state that the ultimate component groups of cellulose are those of the carbohydrates generally and of the sugars in particular—*i.e.*, saturated compounds and derivatives of polyhydric alcohols—generally resistant *i.e.*, non-reactive. But the special chemistry of cellulose has to do with the complex or aggregate. The particular feature of cellulose is that it enters into a number of reactions, combining with other bodies to form highly characteristic derivatives, in which the essential properties of the aggregate are fully maintained. These properties are recognised in the following: (a) the colloidal characteristics of the solutions of the original cellulose, as of its ethereal derivatives; (b) the structural characteristics of the solids obtainable from these solutions by elimination of the solvent; (c) the weight relations of the products, the cellulose maintaining its integrity as a complex. What we have to set forth as a sketch of the special properties of cellulose will follow this order of idea.

I.

Cellulose as a Typical Colloid.—It may be said generally that we know very little of solid substances; it is only in solution or the fluid state that matter lends itself to quantitative analytical investigation. It is in the manifestation of associated properties in solution that compound matter has come to be regarded as falling into two great divisions, Crystalloids and Colloids. Crystalloids are crystalline as solids and when dissolved in neutral solvents constitute limpid solutions; Colloids are non-crystalline or amorphous, and dissolve to viscous or gelatinous solutions. On evaporating the solvent the former resume their crystalline form, the latter constitute structureless masses; these may be transparent, and if spread over a relatively large superficial area they take the form of a film or sheet. A familiar type of colloid is gelatin. Gelatin in 10—20 per cent. aqueous solution at temperatures of 50—100°, is a viscous liquid; the solution on cooling to 20—30° solidifies to a jelly or "gel." The "gel" continues to lose water at its surface and, by withdrawing water from the interior, continues the process of desiccation. The "air dry" solid finally retains

15 per cent. of its weight of moisture, which requires a higher temperature for its expulsion. The dry solid is relatively inelastic or brittle.

There are various views current as to the causes underlying these phenomena. Any such view or "theory of the colloidal state" must set out from the observed experimental facts which are, chiefly: (1) The antithesis between solid crystalline and amorphous matter; (2) the correlatively divergent properties of these two types of matter when in solution: thus, the crystalloids are generally *electrolytes:* they are conductors of the electric current, by which they are readily decomposed, taking up the electrical energy and splitting into polar constituents; the colloids are non-conductors in this sense. The crystalloids are *diffusible, i.e.*, they readily pass through membranes such as parchment, or parchmentised paper—the phenomena being classified under the term *osmosis;* the colloids are not diffusible—that is, exert no osmotic pressure in solution—and consequently are not transmitted through such membranes or films.

The crystalloids, in *dissolving*, undergo *changes of volume*, accompanied by considerable thermal effects: the colloids dissolve with relatively slight volume change. Colloidal matter, when observed in transparent forms, is *optically homogeneous;* crystalline matter exhibits selective actions which are classified under the term polarisation. These effects in certain groups of compounds, *e.g.*, the sugars, persist in their solutions. It is important to note that we have the primary antithesis of solid form, associated with differentiated relationships to the various forms of energy—electricity, heat and light. It must not be assumed, however, that there is any sharp distinction of one form of matter from another: the antithesis is an opposition of extremes, emphasised by the comparison of typical representatives. But these extremes graduate on either side into forms of matter which have the characteristics of both. There is an important deduction from these relationships, which is that throughout the series the ultimate properties of matter are involved as the conditioning factor of the "physical" state. It was formerly held that the antithesis of crystalloid and colloid was of "physical" significance only, that is, depended rather upon proximate relationships than upon the ultimate properties of matter, which are "chemical." We cannot pursue this theme at any length, and we must refer students who aim at more fundamental analysis of phenomena to special treatises, instancing more particularly "Neue Gesichtspunkte zur Theorie der Kolloide" (E. Jordis, Erlangen, 1904), and other critical and experimental contributions which connect the properties of colloids with the modern theory of solutions. As a general text book we need only mention "Grundriss der Kolloidchemie," by W. Ostwald (Dresden, T. Steinkopff). For a general *résumé* of the literature of colloids covering the earlier periods, the "Bibliographie der Kolloide," by A. Müller (Leipzig, 1904, L. Voss), and for present developments the scientific serial "*Zeitschrift für Chemie und Industrie der Kolloide*" (Dresden, Steinkopff). As a general review of the chemistry of cellulose considered as a typical colloid and the probable relationships of its colloidal characteristics to chemical constitution, the student may consult "Researches on Cellulose," II. (1906), Cross and Bevan.

Cellulose is itself insoluble in all neutral solvent liquids.

The "solutions of cellulose" are in all cases solutions of derivatives. There are two main groups of these derivatives:—

(a.) *Colloidal double salts of cellulose* with metallic saline compounds, viz., zinc chloride and cuprammonium. A "solution of cellulose" results from digestion with these reagents in aqueous solution, and the cellulose is separated from these solutions by mere dilution. It is obtained in a gelatinous, hydrated, and of course, structureless form. The precipitated cellulose retains the metallic oxides; but these are readily removed by treatment with acids. The solutions have a high viscosity and the limit of fluidity, for the purpose of the practical applications of these solutions is reached when the percentage of cellulose in solution is 5—7. Higher percentages in fluid solution are attained at the expense of the integrity of the cellulose aggregate, that is, by various processes of hydrolysis; thus, by employing with the zinc chloride various and increasing proportions of hydrochloric acid, or by previous treatment of the cellulose with both acid and basic reagents, which resolve the aggregate by hydrolytic actions. It must be noted that the state of disintegration of the aggregate persists in the reverted product; the cellulose recovered from the solutions by precipitation is more or less degraded in its structural properties.

(b.) *The esters of cellulose* are the derivatives which result from the combination of its OH groups with acid radicals. The most important of these are the Nitrates, or so-called Nitrocelluloses, the Acetates and Benzoates. The Benzoates are of no practical (*i.e.*, industrial) importance. The Nitrates and Acetates are formed by the action of the acids or their anhydrides upon cellulose. The "nitration" or "acetylation" is progressive, and to form derivatives soluble in various neutral liquids the degree of esterification must proceed beyond a certain limit, viz., that represented by the combination of two of the OH groups of the unit $C_6H_{10}O_5$. Actually the derivatives most commonly employed are, in the case of the nitrates, the esters intermediate between the dinitrate and trinitrate; in the case of the acetates, the complete solubility of the ester requires a stage of esterification closely approximating to the production of a triacetate.

The solvents employed are in the case of the nitrates, ether-alcohol, alcohol and camphor, ethyl-acetate, acetone, and variations of these. The acetates are soluble in a more limited range of liquids, of which chloroform is the most important and characteristic; other solvents are acetic acid, phenol, and pyridine. It is important to note that these esters are produced with a necessarily large increase of weight of the product as compared with the original cellulose, resulting from the introduction of the relatively heavy acid or negative group. This will be appreciated from inspection of the equations representing the limiting reactions thus :—

Cellulose. Nitric Acid. Water. Cellulose Trinitrate.

$$C_6H_{10}O_5 + 3\ HNO_3 = 3\ H_2O + C_6H_7O_2\ (NO_3)_3$$

$$162 \qquad (3 \times 63) \qquad (3 \times 18) \qquad 297$$

Cellulose. Acetic Acid. Cellulose Triacetate.

$$C_6H_{10}O_5 + 3\ C_2H_4O_2 = 3\ H_2O + C_6H_7O_2\ 3\ (C_2H_3O_2)$$

$$162 \qquad (3 \times 60) \qquad (3 \times 18) \qquad 288$$

an increase of weight in either case of over 75 per 100 of cellulose.

These combinations, involving such large increases of weight, may take place under regulated conditions, without affecting the structural integrity of the fibre; the esters differing but little in external appearance from the original cellulose.

They now dissolve in their respective solvents to structureless solutions, which are fluid at concentrations of 10—15 per cent. of the ester. It is to be noted from the weight relationship above set forth that these concentrations are in their equivalent of cellulose 6—8 per cent.

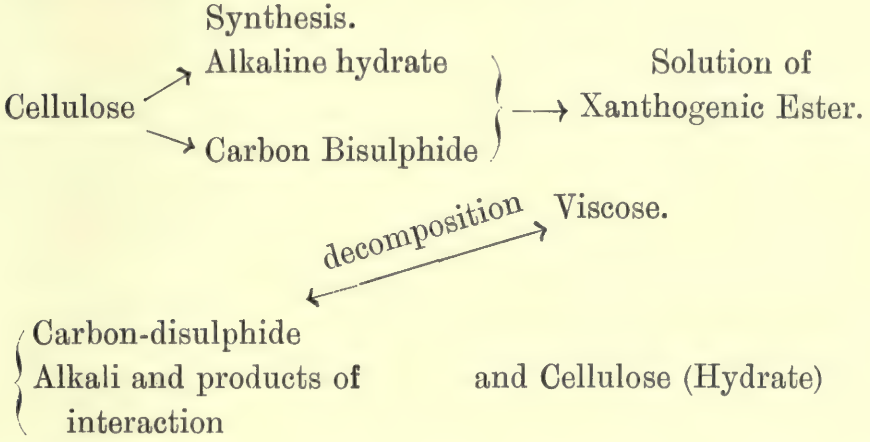
From these solutions the esters are recovered unchanged, by evaporation of the solvent, or by removing it by the action of a liquid, which mixes with the solvent but is not a solvent of the cellulose. From the esters so recovered, the cellulose can only be regenerated by the chemical process of saponification, that is, by the attack of certain alkaline agents which combine with and remove the combined acid groups and restore the OH groups of the original cellulose.

In the industrial uses of these compounds they are sometimes employed as such, or as in the production of artificial silk, the solution being drawn or spun through fine orifices and solidified to the artificial thread which in the case of the nitrate is then denitrated or saponified to cellulose.

The industrial process is therefore in the latter case a complete chemical cycle; the ester stage being, for all practical purposes, merely a solvent-plastic condition of the cellulose.

(c.) Intermediate between these two groups and combining their essential features, is the derivative known as the sulpho-carbonate, or in solution, as viscose. This is a water-soluble ester of cellulose, formed by treating cellulose with strong solutions of the alkaline hydrates, *e.g.*, caustic soda, and the compound so obtained, or alkali-cellulose with carbon bi-sulphide. The ester is thus synthesised in the two stages, and its final form is the sodium salt of cellulose-xanthogenic acid, a compound freely soluble in water. The aqueous solutions of these derivatives (viscose) are structureless, and at cellulose concentrations of 8—12 per cent., are sufficiently fluid for manipulation through filters and for passage through fine orifices under small pressures. (See p. 247.)

The reaction which produces these compounds is a reversible one, and the solutions, on standing, spontaneously revert to cellulose by dissociation of the alkaline sulphur residues. The cycle of synthesis and decomposition may be represented by the subjoined diagram :—



Upon these fundamental facts are based a number of important industrial applications of cellulose.

In the preceding section we have indicated that the cellulose in the form of these soluble derivatives is a structureless colloid. In the plastic condition it may be made to take any desired form, and it is produced industrially in filament or thread, in film or sheet, or, lastly, in massive solids of any required dimensions. The special feature of these artificial forms is a particular continuity of substance. In passing from the state of solution to the ultimate solid form there are no breaks in this continuity, and the structural characteristics of these artificial forms are conditioned by this fact, which, in turn, rests upon the ultimate constitution of the cellulose substance or matter. This finally must be held to be intimately associated with its typically colloidal properties.

The practical effects or consequences of these constitutional properties are seen in the qualities of resistance of the derivative solids. The mechanical properties of the artificial threads, which are expressed in terms of tensile strength or tenacity, extensibility (elasticity), are essential factors of their textile applications. These properties are compared and brought to numerical expression in various ways: thus the tenacity is measured in terms of the maximum weight which the thread will support. As an average figure we may take this as 8,000—9,000 grms. per square millimetre of section. Another mode of expression of the physical fact is in terms of "breaking length," that is, the length of the particular fabric representing such breaking weight. Elasticity is the maximum elongation of the thread under strain from which it will revert to its original dimensions when the strain is removed. This may be 2 to 3 per cent. Extensibility is the elongation of the thread when strained to its breaking point. This varies from 10 to 20 per cent.[1] These cellulose threads are known as "artificial silks," and it is evident from the term, that they are applied to similar purposes as the natural silks. It is of interest, therefore, to compare these products in regard to their fundamental mechanical properties. We quote from a paper on "Cellulose and Chemical Industry" (Cross and Bevan, *Journ. Soc. Chem. Ind.*, 27, 1908).

The comparison with silk is direct and simple, since both represent amorphous colloidal matter or substance.

The artificial silks may be taken as showing the following range of textile quality :—

	Gramme.
[2] Breaking strain or tenacity per unit denier	1·0—1·4
Extensibility under breaking strain	13%—17%
True elasticity	4%—5%

The corresponding averages for the true silks (in the boiled-off state) are :—

Breaking strain or tenacity per denier	2·0—2·5
Extensibility under breaking strain	15%—25%
True elasticity	4%—5%

Strehlenert has established the following relationships, which are important (*Chem.-Zeit.*, 1901, p. 1100).

The breaking lengths are expressed in terms of kilogrammes per square millimetre of section, which is a

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[1] These points are further elucidated in Chap. X.

[2] Denier is the unit weight/length : mgr. per 10 metres.

satisfactory basis of comparison in view of the close structural similarity of the products investigated :—

			Dry	Wet.
“Natural silk.”	China raw silk		53·2	46·7
	French ,, ,,		50·4	40·9
	,, boiled off		25·5	13·6
	,, dyed red, weighted		20·0	15·6
	,, blue black at 110 per cent.		12·1	8·0
	,, ,, ,, 140 per cent.		7·9	6·3
	,, ,, ,, 500 per cent.		2·2	—
“Artificial silks.” Lustra celluloses	Chardonnet	Nitrate process	14·7	1·7
	Lehner		17·1	4·3
	Glanzstoff, cuprammonium process		19·1	3·2
	Viscose, xanthate process		21·5	5·3

The lustra celluloses are thus inferior in tenacity to the silks, but when these are “weighted” there is a loss of strength beyond that which would be directly proportional to the degree of “dilution” of the silk substance.

As the weighting of silks is very largely practised, it will be seen that the lustra celluloses are quite on the average level of textile quality, even in this higher sphere.

In regard to elasticity and extensibility, which are important correlative measures of textile quality, a similar series of relations obtains.

The lustra celluloses, on the other hand, have a special relationship to water, the colloidal cellulose having a considerable hydration capacity. In actual practice this fact is not of such moment as to impede the very rapid progress of the industry in these new textiles.

That this property or relationship of the cellulose is modifiable appears to be a reasonable deduction from the general reactivity of cellulose. It has been presumed by investigators that the cellulose (hydrate) is susceptible of modification, either by intrinsic or constitutional change, or by reaction to form a new derivative, in such a way as to yield a product more nearly resembling the normal cotton cellulose in resistance to hydration. At this date there is only one method which has given promise of industrial results in this desirable direction.

The cellulose, notably in the form of artificial silk, is treated with formaldehyde in aqueous solution containing also auxiliary agents determining combination.

As a result of the combination it appears there is some constitutional change in the cellulose itself accompanying the fixation of the H_2CO groups, and this suggestion is of moment, as it indicates a capacity of internal structural modification which offers an attractive field for research.

It is of particular interest to note that the artificial silks, though produced by treatments of cellulose presenting the widest contrasts in chemical and physical conditions, are closely similar in their properties. It is evident from this that though cellulose is, in chemical language, extremely labile, it is nevertheless so constituted as an aggregate as to be equally stable, or resistant to change.

The reversion of cellulose or of its esters from the solutions above enumerated, in the form of film or sheet, introduces no novel features of the product. The qualities of the film which condition its industrial employment are tensile strength and elasticity.

In the production of solids in massive forms, a number of factors are introduced with the exaggeration of the third dimension, and only one of the solutions, viz., viscose, lends itself to the production of *cellulose* products of this order. The nitrate solutions which are the basis of the highly important celluloid industry are a plastic form of the nitrate or cellulose ester, and the forms into which it is fashioned while in the plastic state are but little different in dimensions from those of the permanent and rigid solids into which they pass by evaporation of the solvent. These are constituted of the unchanged nitrate or cellulose ester. No economical method has been devised for turning out the acid groups from the ester in these massive forms and thus arriving at cellulose in corresponding forms. But the viscose solutions in spontaneously reverting to cellulose and solidifying may be cast, at this stage, into any desired form. The masses so obtained are composed of the cellulose in a much hydrated state ; but though retaining nine times its weight of water (of hydration) it has, nevertheless, a considerable mechanical resistance. Permeated as it is with the alkaline-sulphur by-products, it requires exhaustive washing to remove them. The purified mass of hydrated cellulose, if now dehydrated and desiccated by exposure to the atmosphere, parts with its water continuously and progressively, shrinks upon itself, and finally, is obtained in transparent or translucent masses. The cellulose solid so obtained is an extremely resistant material.

The properties of this material may be compared with those of other solids used in construction, and it will be seen to have qualities of a very high order.

Lastly, we have to call particular attention to the facts which have been generally noted as regards the weight relationships of these cycles of transformations. Taking the two extreme cases, that is, with the widest divergence of the conditions of reaction and with reference to the same unit of cellulose, which we may conveniently take at 100 parts by weight:

Cycle *a*. *Cellulose. Nitrate. Cellulose (hydrate) Acid.*

One hundred parts of cellulose combine with nitric acid (with elimination of water) becoming 165 parts of cellulose nitrate, dissolved in alcohol-ether to 15 per cent. solution (equivalent to 9 per cent. cellulose) and spun to thread, denitrated with ammonium-magnesium sulphydrate, and reverting to 103 parts by weight of cellulose hydrate.

Cycle *β*. *Cellulose. Xanthogenic Ester. Cellulose hydrate. Alkaline.*

One hundred parts of cellulose combine with 50 parts sodium hydrate (in presence of water), the alkali cellulose reacts with 50 parts disulphide, giving 130 parts of cellulose-xanthate of soda dissolved to 13 per cent. solution, equivalent to 10 per cent. cellulose, drawn or spun into "setting" solutions (see p. 246), which decompose the ester and regenerate cellulose, yielding 103 parts by weight of cellulose (hydrate).

In either case, therefore, the cycle is completed without loss of substance by the cellulose: there is a slight gain due to combination with water.

This is only strictly true of the normal cellulose, which is represented by the fully purified cotton fibre. Other celluloses, notably wood-celluloses, sustain a loss of weight due to conversion into permanently soluble derivatives, which may amount to 10—20 per cent. Reciprocally, the viscose cycle becomes a constitutional criterion, a normal cellulose being one which sustains this cycle of reactions of synthesis and decomposition without loss of substance.

These experimental facts define cellulose as a typical colloid. It has, of course, long been recognised in general terms that cellulose in its "organic" forms must be classified as a colloid. But the colloidal state having become a definite objective of investigation, it is evident that the investigation of cellulose through its compounds and derivatives is destined to contribute considerably to the development of the general theory of the colloidal state. For this reason, added to the fact that all the industrial applications of cellulose specially involve its colloidal characteristics, we have limited our present treatment of the subject to this particular aspect.

We now give a brief systematic *résumé* of the properties of cellulose as a chemical individual, these tyyical characteristics being those of cotton cellulose.

Cellulose.—Generally the non-nitrogenous skeleton of vegetable tissues. Type: the fibre-substance of cotton, purified from associated "impurities" by processes of (1) alkaline hydrolysis and oxidation (bleaching); (2) of digestion with hydrofluoric acid, etc., to remove mineral impurity.

Composition.—Elementary $\left\{\begin{matrix} \mathrm{C}\ 44{\cdot}4 \\ \mathrm{H}\ \ 6{\cdot}2 \\ \mathrm{O}\ 49{\cdot}4 \end{matrix}\right\}$ whence the empirical formula $C_6H_{10}O_5$.

Constitution undetermined. Is variously regarded as:—

(1) Polyhexose (anhydride) $<\begin{matrix}\text{Aldose,} \\ \text{Ketose.}\end{matrix}$

(2) Polycyclohexane derivative.

(3) An aggregate of groups of variable and undetermined dimensions, of which only the ultimate terms are known, viz., CH_2OH, CHOH, CO; but the anhydride forms of the alcoholic OH groups, and the position or positions of the CO groups remain undetermined.

Constitutional moisture is retained by the cellulose in its air-dry state, varying between 6 and 8 per cent. according to temperature and saturation of surrounding air.

Solvents.—Cellulose is insoluble in all neutral solvent liquids. Is dissolved by

(1) Concentrated solutions of zinc chloride on heating at 80° to 100°.

(2) Solution of zinc chloride (1 part) in concentrated hydrochloric acid (2 parts) in the cold.

(3) Solution of cupric oxide (hydrate) in aqueous ammonia in the cold. The cellulose may be recovered quantitatively from these solutions, though constitutionally changed.

Reactions.—The above reactions resulting in solution of the cellulose are characteristic; otherwise it is exceptionally non-reactive. By dilute solutions of iodine, in presence of certain dehydrating agents, it is coloured blue.

CELLULOSE COMPOUNDS, *i.e.*, SYNTHETICAL DERIVATIVES.—ESTERS (*a*) NITRATES.—By direct reaction with nitric acid, usually in presence of sulphuric acid, in which case unstable mixed esters are formed as a stage in the reaction, the NO_3 displacing the SO_4H residues. The esters are formed without sensible structural modification. They are purified from residual SO_4H by prolonged boiling with water, and are then "stable." A series of these esters are known, the highest approximating to the trinitrate (C_6) (gun-cotton) the intermediate terms—dinitrate—being soluble in ether-alcohol (collodion cotton), the lowest having physical properties but little different from the original cellulose.

These esters are variously formulated as nitrates of a reactive unit of C_6—C_{12}—C_{24} dimensions.

Solvents.—The special solvents of these esters are acetone, ether-alcohol, nitrobenzene.

Saponification.—By certain alkaline and reducing agents (alkaline sulphydrates) the nitric groups are eliminated and cellulose regenerated.

(*b*) ACETATES.—By reaction with acetic anhydride under various conditions: (1) at 110° direct formation of monoacetate (C_6) insoluble in all neutral solvents and in the solvents of cellulose. (2) At 140° to 160°, formation of higher acetates, attended by solution in the reaction mixture. (3) In presence of catalytic agents ($ZnCl_2$—H_2SO_4—H_3PO_4) at intermediate temperatures; H_2SO_4 determines reaction at 25° to 35°. The products are usually mixtures of tri- and tetracetate. (4) When the reaction mixtures are diluted with hydrocarbon the fibrous cellulose may be acetylated without solution or sensible structural change.

Solvents of the higher acetates, chloroform, acetone, phenol.

Saponification.—The acetyl groups may be removed by boiling with alkaline solutions, the cellulose being regenerated. In quantitative determinations the saponification may be effected by digestion with normal sodium hydrate diluted with an equal volume of alcohol.

(*c*) ACID-SULPHURIC ESTERS.—By the action of sulphuric acid an extended series of esters is formed, which have been described as cellulose sulphuric acids. But they are certainly derivatives of products of resolution. The first stage results in the formation of a disulphuric ester $C_6H_8O_3\,(SO_4H)_2$, but its relationship to the parent complex is doubtful. The ester is soluble in water; the Ca, Ba, and Pb salts are insoluble in alcohol. By progressive hydrolysis the cellulose is ultimately resolved to dextrose.

(*d*) ACETO-SULPHATES AND MIXED ESTERS, containing the SO_4H residues associated with acetyl and other negative groups in combination, are obtained when sulphuric acid is allowed to act under regulated conditions simultaneously with other esterifying agents. Thus a mixture of acetic anhydride (50 parts), glacial acetic acid (50 parts), and sulphuric acid (4 to 6 parts) acts rapidly at 30° to 40°. The first product appears to be a neutral body of the empirical formula,

$$(4\ C_6H_7O)SO_4(C_2H_3O_2)_{10},$$

and under the action of water to undergo an internal hydrolysis, the SO_4 group becoming SO_4H, which forms a stable combination with bases. The Mg, Ca, Zn salts are insoluble in water, but soluble in acetone (see p. 237).

(*e*) BENZOATES result from the action of benzoyl chloride in presence of alkaline hydrates. A monobenzoate (C_6) is obtained by treating cellulose with a solution of sodium hydrate of 10 per cent. (NaOH) strength, and shaking with benzoyl chloride. This benzoate is formed with only slight structural change. The dibenzoate (C_6) is obtained by the interaction of benzoyl chloride and alkali-cellulose (mercerised cotton) in presence of sodium hydrate solution (15 per cent. NaOH). Its formation is attended by structural change; the fibrous cellulose is disintegrated, the dibenzoate being an amorphous substance. The dibenzoate is soluble in acetic acid, chloroform.

Mixed Esters, containing the benzoyl and nitric residues, result from the action of nitric acid upon the benzoates. Simultaneously a nitro-group enters the benzoyl residue.

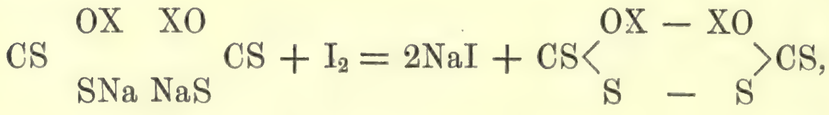
Alkali Cellulose.—The fibrous cellulose undergoes considerable structural modification under the action of solutions of sodium hydrate of 12 to 25 per cent. NaOH. There is a definite synthetical reaction in the ratio $C_6H_{10}O_5$: 2 NaOH, which is a stage in the formation of the dibenzoate (*supra*).

The compound is completely dissociated by water: by treatment with alcohol an equilibrium is reached when the reagents are associated in the ratio $C_{12}H_{20}O_{10}NaOH$.

The alkali-cellulose hydrate, of composition

$$\left.\begin{array}{lr}\text{Cellulose . . .} & 30\\ \text{Sodium hydrate .} & 15\\ \text{Water . . . .} & 55\end{array}\right\}\begin{array}{ll}\text{Cellulose :} & \text{Sodium hydrate,}\\ C_6H_{10}O_5 & 2\,NaOH\end{array}$$

is the first stage in the synthesis of *cellulose xanthogenic* acid, which results from the interaction of the alkali cellulose and carbon disulphide at ordinary temperatures. The sodium salt is soluble in water. It is an unstable compound. the solution undergoing spontaneous progressive change. The solution, which is highly colloidal, finally solidifies. By reason of the characteristic reaction of the xanthates with iodine,



$$CS\begin{array}{l}OX\quad XO\\ SNa\ NaS\end{array}CS + I_2 = 2NaI + CS\left\langle\begin{array}{c}OX - XO\\ S\ -\ S\end{array}\right\rangle CS,$$

the progress of the change may be followed, the essential feature being the elimination of the CS_2 residues with reaggregation of the cellulose units. Well-marked stages in the series occur at the points denoted by the empirical formulæ $C_{12}H_{19}O_9CSSNa$. The former represents an equilibrium attained after the solution has remained for some hours at the ordinary temperature: the latter is reached in from three to four days. The cellulose under the reaction acquires a more acid character, an additional OH group combining with alkali. The lower terms of the series, though insoluble in water or dilute saline solutions, are dissolved by the addition of sodium hydrate. The sodium atom in combination with the CSS residue is not attacked by weak acids, such as acetic acid. By double decomposition with soluble salts of Cu, Zn, etc., the corresponding xanthates are produced as insoluble colloidal precipitates.

In the above reactions the cellulose aggregate is maintained; the solutions of the derivatives are viscous and colloidal; but the following

Reactions of decomposition, which are determined by hydrolytic and oxidising agents, the directions of resolution are extremely various and the relationships of the products to the original aggregate are undetermined.

(a) SULPHURIC ACID, sp. gr. 1·55—1·65, dissolves the cellulose as a disulphuric ester; but decomposition attends the reaction, and on diluting and boiling the hydrolysis is carried to the extreme molecular limit, the final product being dextrose.

(b) HYDROBROMIC ACID in ethereal solution attacks the cellulose profoundly with production of brom-methyl furfural. The formation of this compound indicates a previous or intermediate stage in which the products of resolution are molecular ketonic bodies of carbohydrate constitution.

(c) HYDROCHLORIC ACID in presence of water, dilute sulphuric acid, and acids generally, attacks the cellulose aggregate with production of a variety of derivatives. (1) *Insoluble:* These are generally termed hydrocelluloses. They are disintegrated residues of the original fibres; they differ chemically from the parent aggregate in the presence of free aldehydic groups, and in readily yielding to the action of alkalis. (2) *Soluble* molecular products, chiefly dextrine and dextrose.

(d) ALKALINE HYDRATES and ALKALIS generally have little action on cellulose in the form of dilute solutions—even when treated at elevated temperatures. Sodium hydrate in solution of concentrations of 12 per cent. NaOH and upwards, combines with the cellulose, producing profound structural modifications (mercerisation), but without resolving the aggregate.

At higher concentration and temperature the cellulose is partially dissolved; but even under the conditions of a "fusion" at 180° the resolution is limited to the conversion into alkali soluble modifications, which are precipitated in the colloidal form on diluting and acidifying. At higher temperatures (250°) and with larger proportions of the alkaline hydrates, the cellulose is resolved into acid products of low molecular weight, chiefly acetic acid and oxalic acid.

Oxidants.—The directions of oxidation of cellulose are likewise extremely diversified. The aggregate manifests considerable resistance to alkaline oxidants in dilute form, *e.g.*, solutions of the *hypochlorites, permanganates;* but when the limit is passed the oxidations which result are drastic in the sense that the soluble products are of low molecular weight, chiefly carbonic and oxalic acids. The insoluble fibrous residues, more or less disintegrated, are known as oxycelluloses. They contain free aldehydic groups, are easily attacked by hydrolysing agents, and on boiling with hydrochloric acid (1·06 sp. gr.) are decomposed with production of some furfural.

Resolved by the action of *concentrated* solutions of the *hypochlorites*, cellulose yields chloroform and carbon-tetrachloride. The hypobromites give the corresponding bromine derivatives. Nitric acid (1·25 sp. gr.) at 180° converts cellulose into a series of "oxycelluloses," which are resolved on boiling with calcium hydrate into acid products, among which isosaccharinic and dioxybutyric acids have been identified. In the original oxidation small quantities of the higher dibasic acids—saccharic and tartaric acids—are produced, but the main products are oxalic and carbonic acids.

With *chromic acid* an endless series of oxidations may be effected, the degree of action depending upon the proportion of the active oxidant and the associated hydrolytic action of mineral acids. The oxycelluloses produced are distinguished by relatively large yield of furfural when decomposed by boiling HCl Aq (1·06 sp. gr.). In presence of sulphuric acid there ensues complete combustion, and the reaction is the basis of quantitative analytical methods.

Resolution by Ferment Actions.—Under the actions of specific organisms the cellulose complex is totally resolved, the main products being methane, hydrogen, and carbonic and fatty acids. The decomposition may be associated with the action of an enzyme; but a remarkable feature of the process is the absence of intermediate products, at least in the cases hitherto investigated. In the digestive tract of the herbivora cellulose is resolved, and from the investigation of the process, necessarily by indirect observations, it appears that, in addition to a destructive resolution to ultimate gaseous products, there occurs a resolution to proximate groups of high nutritive value, which are assimilated by the animal organism.

Resolution by Heat; Destructive Distillation.—The decompositions of cellulose at temperatures exceeding 250° are necessarily extremely complex.

The groups of products show an average production:

Solid 30 per cent.	Liquid 50 per cent.	Gaseous 20 per cent.
Charcoal or pseudo-carbon	Containing Acetic acid (2 per cent.) Methyl spirit (7 per cent.) Acetone, furfural tar (12 per cent.)	Chiefly CO and CO_2

the actual proportions and composition of these mixtures varying with the temperature and duration of the heating.

General View of the Decomposition of Cellulose.—It is clear that the cellulose complex breaks down under destructive influences, in directions depending upon the nature of the attacking agent, its concentration, and all the surrounding physical conditions. The study of these decompositions has thrown but little light on the actual nature and constitution of the cellulose aggregate; for the reason, perhaps, that we have endeavoured to maintain a basis of interpretation such as is applicable to ordinary molecular compounds or complexes. If we regard cellulose as the analogue of a complex salt in presence of water, and endeavour to follow the reactions of decomposition as we should the changing equilibrium of a *colloidal salt solution* under the action of reagents, we have a basis of working hypotheses which will be found to stand the general test of credibility—that is, they tend to progress in investigation. We make this observation in reference to the matter which we have just endeavoured to reduce to short, systematic expression, but which obviously cannot effectually be so treated, because it involves the entire theoretical basis of our subject—that is, the actual state of matter and the distribution of the reactive unit-groups in the cellulose complex; and this basis is as yet entirely undetermined.

The Cellulose Group.—From the typical cellulose we pass to the diversified *group of celluloses.* Their general characteristics are those of the prototype; the variations they present are especially such as involve the undetermined factors of constitution. With these there are certain correlative variations which afford an empirical basis of classification. These are (a) the degree of resistance to hydrolytic and to oxidising agents, (b) the percentage yield of furfural when decomposed by boiling HCl Aq, (c) elementary composition, in respect of the ratio C : O.

The fibrous celluloses are grouped as follows:—

Type.		Cotton sub-group A Bleached cotton.	Wood cellulose sub-group B Jute cellulose.	Cereal cellulose sub-group C Straw cellulose.
Elementary Composition	(C)	44·0—44·4	43·0—43·5	41·5—42·5
	(O)	50·0	51·0	53·0
Furfural . .		0·1—0·4	3·0—6·0	12·0—15·0
Other characteristics . .		No active CO groups.	Some free CO groups.	Considerable reactivity of CO groups.

Of these groups the following points may be noted :—

A.—Comprises, in addition to cotton, other industrially important celluloses, *e.g.*, flax, hemp, and rhea. They occur in the plant world in association with compounds easily removed by the action of alkalis. They pass through the cycle of reactions involved in their solution as xanthate, without hydrolysis to soluble derivatives.

B.—These celluloses are obtained as products of decomposition of a compound cellulose. They may be regarded as partially hydrated or hydrolysed. They are more readily attacked by hydrolysing agents and, in the xanthate reactions, are partially resolved to alkali-soluble derivatives.

C.—These celluloses are in most cases a complex of structural elements, and not homogeneous chemically. They are still less resistant than the preceding group, and more especially the furfural-yielding components, which are selectively attacked under certain conditions.

The cellulose groups, as above, pass by imperceptible gradations into a heterogeneous class of natural products which, while possessing some of the characteristics of the celluloses proper, are so readily resolved by hydrolytic treatment that they must represent a very different constitutional type or types. To this group of complex carbohydrates the class-name *hemicellulose* has been assigned. They are structurally different from the fibrous celluloses, occurring mostly in the cellular form (parenchyma, etc.). They differ in physiological function and in being readily resolved by hydrolysis into the crystalline monoses.

II.

We have now to deal with the complex of groups in combination with the cellulose in the ligno-celluloses. They are conveniently grouped under the neutral term "non-cellulose"; but in view of their leading characteristics, which are those of the di-ketones, or more particularly quinones, they are more aptly described by the term "lignone."

A ligno-cellulose as a compound of cellulose and lignone is differentiated from cellulose in many important respects. First, in elementary composition it presents a striking contrast, as will be seen from the subjoined numbers :—

	Cellulose.	Typical Ligno-celluloses.		
		Jute.	Pinewood.	Beechwood.
Carbon . .	44·4	47·0	48·4	49·1
Hydrogen .	6·1	6·1	6·3	6·2
Oxygen . .	49·5	46·9	45·3	44·7

Applying a statistical calculation to one of the ligno-celluloses, we may conclude that the lignone complex is a body of much higher carbon contents (57 per cent.) than cellulose (44 per cent.). Thus :—

			Carbon.
Ligno-cellulose Jute	Cellulose	$\frac{75 \times 44}{100}$	33·00
	Lignone	$\frac{25 \times 57}{100}$	14·25
			47·25

Further we may calculate from the figures that the ratio of the elements in the lignone is approximately $C_6 : H_6 : O_3$ expressed on a C_6 unit.

Two reactions of the lignone are of importance in enabling us to fix this empirical formula more closely, as well as certain constitutional relationships.

Chlorine.—The lignone reacts quantitatively with chlorine, combining with the halogen, that is, in a characteristic and invariable proportion. In the case of jute this proportion is 8 per cent. of the ligno-cellulose, and an equal proportion is converted with hydrochloric acid. In the woods, the chlorine combining is higher in proportion to the higher percentage of lignone groups; but the hydrochloric acid produced is much higher. The chlorinated complex is soluble in certain neutral solvents, such as alcohol. The analysis of the chlorinated derivative obtained from jute establishes the formula $C_{19}H_{18}Cl_4O_9$, and the investigation of the reaction has shown that the lignone is integrally attacked. The chlorinated derivative reacts with sodium sulphite in aqueous solution, and is converted into a soluble sulphonated derivative, being quantitatively eliminated from the cellulose. This reaction is employed for the quantitative resolution of the ligno-cellulose and the estimation of its cellulose contents. The chlorinated group in the lignone derivative is identified as a quinone chloride, and the complex thereby definitely connected with the aromatic or benzene group of carbon compounds. The chlorinated group is converted by treatment with nascent hydrogen (zinc and sulphuric acid) into a derivative of pyrogallol; and the complex is thus closely related to the "tannins," of which the trihydroxybenzenes are as characteristic constituent groups. Incidentally it has been shown that the lignone complex, in further contrast to cellulose, contains but a small proportion of free hydroxy groups.

Bisulphites.—The lignone reacts integrally and selectively with the bisulphites of the alkali and alkaline earth metals;

a ligno-cellulose treated with solutions of these compounds at elevated temperatures and under pressure is quantitatively resolved into cellulose obtained as an insoluble residue of the ultimate fibres, and soluble sulphonated derivatives of the lignone. This process is not only quantitative, but fulfils the further requirements of an economical industrial process, and it is therefore extensively employed in the preparation of wood cellulose or wood pulp from the woods of the coniferæ. As an industrial process it will be fully described in a subsequent chapter. At this point we are concerned with the nature and composition of the soluble by-products, which are, in effect, the lignones in combination with the bisulphite residues. These compounds have been separated in various derivative forms and analysed, and the following empirical formulæ have been established :— (*Cellulose*, pp. 200, 201).

From analyses of product precipitated by hydrochloric acid

$$C_{24}H_{24}(CH_3)_2SO_{12}.$$

From analyses of compounds obtained by precipitation with lead oxide

$$C_{24}H_{24}(CH_3)_2SO_{12}.$$

Brominated derivative

$$C_{24}H_{22}(CH_3)_2Br_4SO_{11}.$$

The parent molecule or lignone complex of the wood may be taken to have the composition

$$C_{24}H_{24}(CH_3)_2O_{10}.$$

The above reactions of the lignone complex are specially characteristic; they are simple and quantitative, and as they are devoid of secondary complications, the derivatives are in simple relationship to the parent complex. But the more complete characterisation of the lignone is necessarily based upon the study of reactions of decomposition.

These are, however, extraordinarily complex, and in accordance with our present treatment of the subject, our description will be limited to a general outline.

Chromic Acid in presence of a hydrolysing acid attacks the lignone complex in the cold. The reaction has been specially studied in the case of jute. The important features of the decomposition is the complete breakdown to acid products of the lowest molecular weight—carbonic, formic, acetic and oxalic acids. This bears a direct interpretation in reference to the constitution of lignone; it excludes hydrocarbon nuclei of any but the smallest dimensions, notwithstanding the large dimensions of the lignone formula; and further implies a relatively high proportion of CO groups, alternating in periods of short dimensions with hydrocarbon groups. When the reaction is applied to the ligno-cellulose the action is confined to the lignone, so far as it may be described as a destructive oxidation, but extends to the cellulose in converting it into an "oxycellulose" largely soluble in alkaline solutions.

Nitric Acid attacks the ligno-celluloses at all concentrations and temperatures, and under most conditions effects a destructive resolution of the lignone. The following are the results of a statistical investigation of the decomposition of jute ligno-cellulose:—

Ligno-cellulose and Nitric Acid (10% HNO_3) at 60—80°.

	Cellulose α.	Oxalic acid.	Complex unstable acid.
Solid products .	63—56%	40—55%	
Volatile products .		Acetic and Formic acids (14—18%)	
Gaseous products .	From HNO_3		From Ligno-cellulose
	N_2O_4,N_2O_2,N_2O,N_2.HCN		CO_2—CO—HCN

Cellulose α is a more stable and resistant cellulose by contrast with cellulose β which is attacked under the above conditions, though resistant to chlorine, and therefore to the conditions of the process described on p. 59.

This reaction has been the subject of various patents and attempts to develop upon it an industrial process for the preparation of cellulose.

As regards the theoretical bearings of these results, the far-reaching resolution of the lignone under an attack which cannot be described otherwise than as of very moderate intensity, further confirms the conclusions as to the prevalence of CO groups in the lignone complex, alternating with hydrocarbon groups of relatively small dimensions. Of other acid resolutions we shall mention as yielding characteristic products:

Hydrochloric Acid.—The aqueous acid at a concentration of 12 per cent. HCl (sp. gr. 1·06) determines a highly complex series of changes at the boiling point. Both the cellulose and lignone are profoundly attacked. The characteristic product is the volatile aldehydic substance furfural, which distils, and may be quantitatively estimated in the distillate. The yields of this aldehyde are characteristic of the various types of ligno-celluloses:—

Average yields of furfural from typical ligno-celluloses.	Jute	8·0
	Beechwood . . .	18·0
	,, purif. Alkalis	12·0
	Coniferous woods .	4·0—5·0.

It may be noted that the furfural-yielding constituents of the ligno-cellulose occupy an intermediate position in function and relation between the lignone and cellulose. Thus in isolating the cellulose by the chlorination process, a cellulose is obtained which yields 6—8 per cent. furfural on boiling with the acid ; this cellulose is the β cellulose mentioned on p. 61. Further, on treating the ligno-celluloses with alkaline hydrates in the cold, a constituent is dissolved, which is separated on acidifying the solution, as an amorphous colloidal precipitate. Beechwood yields this product in exceptional proportion. It is known as wood gum. It is characterised by its high yield of furfural, viz., 33—48 per cent. according to its degree of "purity," *i.e.*, the freedom from associated groups of the characteristic component. This body is a "Pentosan," an anhydride of the C_5 sugars, an analogue of starch, which may be regarded as an anhydride of the C_6 sugar dextrose. These C_5 sugars do not occur free in the plant world ; but in the form of these amorphous and colloidal anhydrides are very widely distributed as constituents of plant tissues. The condensation to furfural as a main reaction, though characteristic of these C_5 sugars, is not an exclusive constitutional index, and there are many possible groupings which might undergo this condensation. It is therefore usual to adopt the more general term of furfuroid in describing such plant or constituents as yield furfural; the narrower identification as a pentosan depends upon the actual production of the C_5 sugars as products of hydrolysis.

Alkaline Decompositions.—The lignone group is attacked by alkaline solutions at elevated temperatures and converted into soluble derivatives, which are acid in character, but for the most part of ill-defined constitution. The cellulose, resisting the action of these reagents, is separated and is obtained as a disintegrated mass of fibrous or cellular units, constituting a "pulp." Upon these decompositions are based an important group of industrial processes for the preparation of wood pulps, which will be found described.

Having by this discussion obtained a general knowledge of the ligno-celluloses as chemical compounds, and also of the ultimate component groups of both lignone and cellulose, we are in a better position to deal with certain special properties and reactions of the ligno-celluloses, either involved in the industrial applications of those products which they to some extent define and limit, or employed in their quantitative estimation when present as constituents of a fibrous mixture.

Some of the characteristic reactions of the ligno-celluloses, about to be described, appear to be due to actual furfural derivatives present in the complex. The pentosans, on the other hand, if assumed to be the mother substance of the furfural obtained, are saturated derivatives, and their composition and properties are such as would leave many of the characteristics of the lignone complex unaccounted for.

Hydriodic Acid decomposes the ligno-celluloses with liberation of methyl iodide, and the production and estimation of this volatile product, is taken as the index and quantitative measure of methoxyl OCH_3 groups present in the ligno-cellulose. This ethereal group is a further "chemical constant of lignification." The percentages of ethereal methyl groups are remarkably uniform for a very large range of woods or ligno-celluloses. The following have been determined (Cellulose, p. 189):—

A. Woods.

			CH_3 p.ct.
Maple	Stem	*Acer Pseudo-platanus*, L.	3·06
,,	,, extracted[1]	,, ,,	3·05
,,	,, shavings	,, ,,	3·06
Acacia	Branch	*Robinia Pseud-Acacia*, L.	2·37
,,	Extracted	,, ,,	2·45
Birch	3 years old	*Betula alba*	2·57
Pear	Stem	*Pyrus communis*, L.	3·21
Oak	,,	*Quercus pedunculatus*	2.86
,,	,,	,, ,,	2·63
Alder		*Alnus glutinosa*	2·89
Ash	Stem	*Fraxinus excelsior*, L.	2·71
,,	Shavings from stem	,, ,,	2·69
,,	Stem shavings extracted	,, ,,	2·66
,,	Shavings from branches	,, ,,	3·02
,,	Shavings from branches extracted	,, ,,	2·91
Fir	Stem	*Abies excelsa*	2·15
,,	,,	,, ,,	2·25
,,	,,	,, ,,	2·39
,,	,, (central zone)	,, ,,	2·59
,,	,, (sap wood)	,, ,,	2·32
,,		*Abies pectinata*, DC.	2·45
Pine		*Pinus sylvestris*, L.	2·25
,,	Stem	*Pinus laricis*	2·05
,,	,,	,, ,,	2·12
Cherry	,,	*Prunus Avium*, L.	2·38
Larch	,,	*Larix europæa*, DC.	1·99
,,	,,	,, ,,	2·68
Lime	,,	*Tilia parvifolia*	2·56
Mahogany	,,	*Swietenia Mahagoni*, L.	2·66
Walnut	,,	*Juglans regia*, L.	2·27
,,	Shavings from stem	,, ,,	2·69
Poplar	Stem	*Populus alba*	2·59
Beech	,,	*Fagus sylvatica*	3·02
,,	,,	,, ,,	2·62
,,	,, shavings	,, ,,	2·70

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[1] "Extracted" signifies previously exhausted with water, alcohol, and ether. Otherwise the specimens were analysed without previous preparation.

			CH_3 p.ct.
Elm	Stem	*Ulmus campestris*	2·92
,,	,, shavings extracted	,, ,,	2·75
Willow		*Salix alba*	2·31

B. Fibrous Products.—Natural and prepared.

Jute (*Lignocellulose*)		1·87
Swedish filter paper		0·0
Cotton		0·0
Flax, unbleached	*Linum usitatissimum*	0·0
Hemp ,,	*Cannabis sativa*	0·29
China Grass, unbleached	*Böhmeria nivea*	0·07
Sulphite (*Cellulose*)	*Pinus sylvestris*	0·34

C. Miscellaneous.

Cork	*Quercus suber*	2·40
,,	,, ,,	2·47
Nutshells	*Juglans regia*	3·74
Lignite (Wolfsberg)		2·44
Brown coal		0·27

In reference to actual molecular proportions it is to be noted that in the sulphonated derivatives obtained from the lignones of coniferous woods the proportion is indicated by the formula $C_{24}H_{24}(CH_3)_2SO_{12}$. The localisations of these methyl groups is a present object of investigations; and their presence is established in the celluloses isolated from the ligno-celluloses. This is taken as an indication of a genetic relationship between cellulose and lignone.

We may now set out the main features of the chemistry of the ligno-celluloses in a brief *résumé* as follows:—

With the typical characteristics of the celluloses as complex aggregates, the ligno-celluloses similarly react with the zinc chloride reagents to form colloidal solutions; also to form esters with nitric acid, acetic anhydride and benzoyl chloride, respectively nitrates, acetates, and benzoates. But such reactions are in the main those of the cellulose constituents of the complex, the latter remaining unresolved. The lignone groups with which the cellulose is combined or associated are sharply differentiated from the cellulose not only by higher carbon percentage and low molecular proportion of OH groups, but by constitution; they are unsaturated, cyclic compounds, and hence react synthetically with chlorine, bisulphites and nitric oxides.

They are greedy of oxygen, and are profoundly attacked by all oxidising agents, are even subject to progressive attack by atmospheric oxygen. Hence the ligno-celluloses as constituents of papers lower the qualities of these important industrial products, not only from their inferior intrinsic paper-making quality, but from the changes which take place as a result of atmospheric oxidation: these are, discoloration and loss of tenacity. Cellulose, as a saturated compound, is free from this cardinal defect, and we have practical evidence of this in the extraordinary resistance to atmospheric influences of papers and textiles which have been preserved to us from the Middle and earlier ages.

Associated with these constitutional features we have a well marked and diversified dyeing capacity: the ligno-celluloses are dyed easily and by colouring matters of widely varying constitution, whereas the celluloses proper have a selective or limited tinctorial capacity.

As regards intrinsic "colour," the ligno-celluloses occur in forms which would be described as grey, yellow or brown —but such colours are mostly due to associated by-products.

When freed from these by certain standard methods of "bleaching" they assume a bright cream to whitish colour. But bleaching processes are based upon alkaline and oxidising treatments, to both of which the lignone constituents are extremely sensitive. Hence the limitations of ligno-cellulose textiles, such as jute, in respect of colour. The substance will not sufficiently resist the necessary treatments for a "high bleach." Another feature of inferiority is a joint product of the relative shortness of the ultimate fibre and want of resistance to the chemical actions of hydrolysis and oxidation. From a practical point of view the ligno-celluloses are composed of cellulose units of short dimensions (1—3 mm.) cemented together by the lignone components. When these are removed the fibre is disintegrated; for it is evident that structural units of $\frac{1}{8}$ in. length cannot cohere, and the strength of a yarn or fabric presenting this condition can only be that due to the adhesion of the fibres, as in a sheet of paper. When wetted the adhesion is reduced to a fractional proportion. Hence the bleaching of ligno-celluloses is a matter of practical compromise, and a ligno-cellulose fabric, bleached or unbleached, is always tending, however slowly, to disintegration, as a result of the attack of the natural and all-pervading agencies oxygen and water.

It is necessary for a thorough grasp of the chemical technology of the woods, to take the logical road of studying the jute fibre as a structural type, and the jute fibre-substance as a typical ligno-cellulose. From the latter point of view it occupies the mean position between the celluloses and the perennial woods, and it will be found to be generally true of the characteristic reactions of these substances. Thus jute is attacked by the cuprammonium reagent and for the most part dissolved; but the ligno-celluloses of the woods are scarcely affected. Strong solutions of the caustic alkalis produce the effects of "mercerisation" upon jute and fibrous ligno-celluloses of similar composition, but not upon the woods. Moreover, if mercerised jute, retaining the soda (NaOH) be exposed to carbon bisulphide, synthesis of a xanthogenic acid occurs, as with the celluloses. But the reaction is complicated by the presence of the lignone groups, and the product, instead of being entirely soluble to a structureless solution, is swollen or distended by water to practically indefinite limits, and after being so distended, if then decomposed it reverts to a fibrous mass. In the case of the woods, on the other hand, there is no perceptible attack even on prolonged joint action of the alkali and carbon bisulphide. The higher proportion of lignone constituents in the woods, with decreased percentage of cellulose, has the effect, therefore, of producing a condition of resistance to reaction, or chemical inertness. Doubtless this is related to the physiological functions of the woods and their persistence during the prolonged period of life of trees; and this property of inertness is attained by increase in groups which are highly reactive and extraordinarily "labile." The result appears to be paradoxical, and involves a natural equilibrium of obviously profound significance.

This will be more fully appreciated from a consideration of certain characteristic colour reactions of the ligno-celluloses, which are a certain measure of, being quantitatively related to, their lignone constituents.

Ferric Ferricyanide.— The red solution which results from the interaction of ferric salts and alkaline ferricyanides in solution thus:—

$$FeCl_3 + K_3FeCy_6 = 3\ KCl + Fe_2Cy_6$$

colours the ligno-celluloses a deep blue as a result of deoxidation of the ferric compound and reduction to the complex cyanides known as Prussian blue, Turnbull's blue, etc. These separating as colloidal hydrates are deposited in a state of intimate union with the ligno-cellulose substance, and in the case of the jute fibre it is easy to see by microscopic examination that the colloidal blue pigment is structurally incorporated with the fibre substance. The amount so combining may be 30—40 per cent. of its weight, without changing the external characteristics of the fibre, *i.e.*, form and lustre. The reaction is of use in following the progressive elimination of the lignone constituents in the processes of isolating cellulose.

Students who wish to follow up this interesting reaction are referred to *Journ. Soc. Chem. Ind.*

Phenols. — The aldehydic and ketonic constitution of the ligno-celluloses determines characteristic reactions with aromatic hydroxy derivatives or phenols. One of these is exceptionally striking.

Phloroglucol, the symmetrical trihydroxybenzene ($C_6H_3 . O^1H . O^3H . O^5H$) in solution in aqueous hydrochloric acid of 1·06 sp. gr. reacts with production of coloured derivatives of magenta-red hue.

The depth of colour developed is constant for any given ligno-cellulose, and may be used as a quantitative estimation of ligno-celluloses in intimate admixture with non-reactive substances such as cellulose.

Ordinary printing papers are a mixture of "ground wood" pulp, and "chemical" pulp or cellulose, and the depth of coloration obtained in moistening with the "phloroglucol reagent" affords an approximate measure of the proportion of the former or ligno-cellulose.

A closer study of the reaction has shown that it consists of two phases; the coloured bodies result from a minor reaction reaching a maximum with less than 1 per cent. of the phenol per 100 parts of the ligno-cellulose: the major reaction takes place without development of colour and "fixes" a further 6—7 per cent. of the phenol in combination as a product of condensation. The colour-reactions appear to be due to aldehydes of the furfural type, probably hydroxy furfurals.

As a result of this further investigation a more strictly quantitative method has been devised which measures the total phenol combining, and by calculation the proportion of ligno-cellulose in mixtures. (See *Ber. Deuts. Chem. Ges.*, 40, 3119, 1907.)

Aromatic Bases, such as aniline and substituted anilines react with constituent groups of the ligno-cellulose complex, giving characteristic yellow to orange colorations.

With dimethylparaphenylenediamine the reaction is more striking, the colour developed being a "magenta" red. With the ligno-celluloses in their normal state the colorations are constant, and are therefore an approximate quantitative measure of the proportion of ligno-cellulose in admixture with non-reacting substances such as cellulose. The method devised by Wurster consists in developing the colour reaction and comparing the depth of colour with a graduated scale of fixed tints.

It is to be noted again that these reactions are not characteristic of the ligno-cellulose as such. They are weakened by treatment of the ligno-celluloses with reagents of feeble intensity, such as sulphurous acid and sulphites under conditions which leave the ligno-cellulose itself unaffected. They are reactions, as in the case of the phenols, with by-product groups, invariably present. There is evidence that these groups are the same as those which react with the phenols. (See also *Ber. Deuts. Chem. Ges.*, 40, 3119.)

Ligno-cellulose and Photo-chemical Phenomena.

We cannot close this theoretical account of the ligno-celluloses without introducing the researches of the late W. J. Russell on "The Action of Wood on Photographic Plates in the Dark" (*Phil. Trans. B.*, 197, 281, 1904; also *Proc. R. S. B.*, 78, 385; 80, 376).

We are indebted to Mr. W. F. Bloch, who assisted Dr. Russell in these investigations, for the following notes of their results:—

Russell found that all the woods were able to give definite pictures upon a photographic plate, in absence of light.

The action takes place when the wood is kept at a considerable distance from the plate; but for perfect definition, contact was necessary. The pictures usually corresponded with the visible structure of the wood; but in some cases there was a marked differentiation.

This selective activity appeared to depend in part upon the resinous constituents of the wood and its disposition on the cells; but also in part upon the nature of the cell-wall structure itself, which in cases offered much resistance to the passage of the active bodies.

On the evidence the active bodies must be regarded as an emanation, but differing entirely from radio-active emanations.

All the properties ascertained identify the substance with hydrogen peroxide.

Ordinary photographic dry-plates may be used to produce this effect; care must be taken to select such as have been preserved in wrapping materials themselves unable to act upon the plates.

The action takes place slowly at ordinary temperatures (one day to twenty-one days) according to the nature of the specimen, but rapidly at 50—55° C. (half to eighteen hours).

The shorter exposures give sharper pictures, which observation accords with the conclusion that the active body is of the nature of a vapour or volatile compound.

Bark and pith structure are almost inactive. Within the bark there is a bark-forming tissue, which gives alternate layers of active and inactive tissue. The latter was also found to have the property of being impervious to hydrogen peroxide.

The activity of the woods is increased in all cases by exposure to strong light, and observations on the spectrum showed that the blue end was particularly active.

The increased activity disappears on keeping the specimens after exposure in the dark.

Resinous substances extracted from a number of woods were found to be all more or less active. Para-abietic acid was prepared and found to be particularly active. It is

Action of wood on photographic plate in the dark (W. J. Russell, Phil. Trans. B. 197—281).

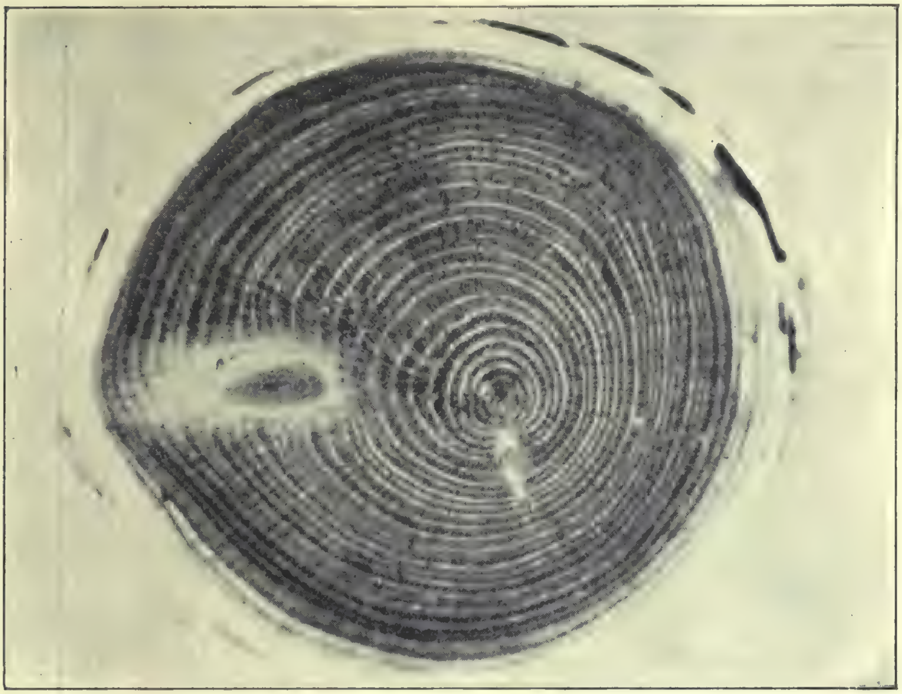

Fig. 13b.—Oak.

Fig. 13a.—Larch.

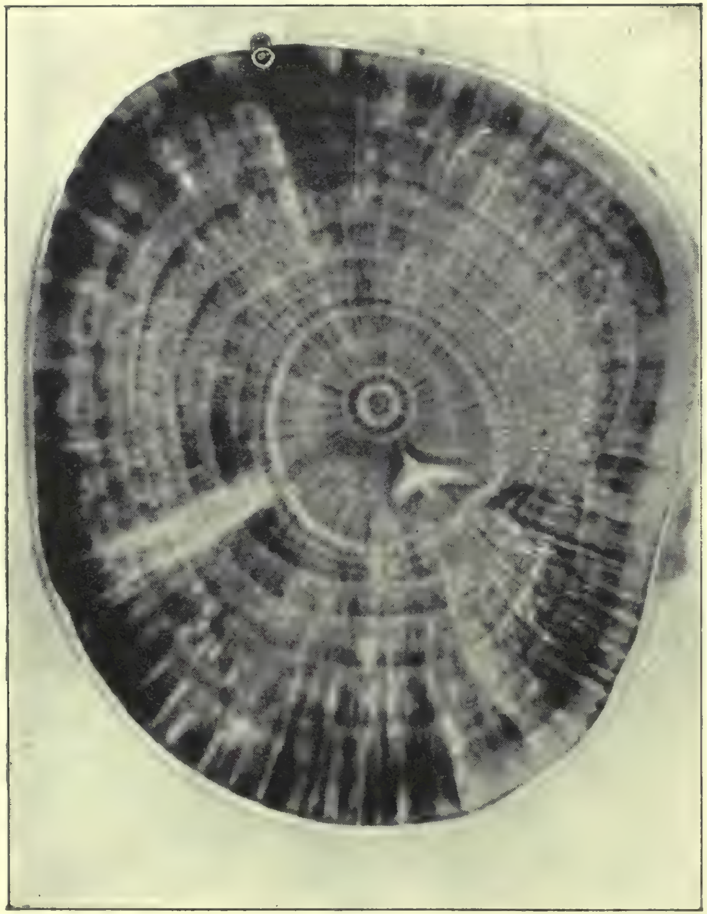

FIG. 13C.—Spruce.

FIG. 13D.—Scotch Fir.

well known that this body shows the phenomenon of autoxidation, which is no doubt associated with its unsaturated constitution.

The fossil resins show slight activity; coal also shows activity, and attempts were made to apply this to the identification of different types of coal.

Woods were exhaustively treated with resin solvents, but were found to be still active, and the evidence goes to show that we are dealing with a definite property of the ligno-celluloses.

It is to be noted that a short exposure to steam or to chlorine gas renders the wood substance inactive.

The action is arrested in an atmosphere of carbonic gas, but is stimulated by the presence of oxygen.

Experiments in which the active substance in sufficient mass was swept with a stream of air, and the current of air afterwards made to act upon a photographic plate at some distance, showed that the active substance could be carried forward.

It was also found that diaphragms carrying any substance capable of absorbing and destroying hydrogen peroxide arrested the action.

The investigation is still at this empirical stage. Russell has left an interesting legacy of highly suggestive observations, and the matter invites further investigation, as the exploration of the causes is calculated to throw a very important light on the natural chemical equilibrium of the ligno-celluloses.

CHAPTER III

WOOD PULPS IN RELATION TO SOURCES OF SUPPLY: FOREST TREES AND FORESTRY

The use of wood pulp as a raw material for the manufacture of paper is of comparatively recent origin, its commercial application for this purpose dating from 1869, when about 60 tons of mechanical-ground wood pulp were exported from Norway to England. In the following year the quantity rose to 500 tons, and from that year onward the industry has grown by leaps and bounds, the total amount of wood pulp imported in 1909 being over 500,000 tons.

At the present rate of consumption of wood for papermaking, the devastation of forest areas has become so serious a matter that the Governments of the various countries in which these forests exist are taking vigorous steps in the first instance to prevent their absolute destruction, but further to secure a systematic upkeep.

It is very difficult to arrive at accurate figures representing the world's production of wood pulp; but from the semi-official published returns an approximate estimate may be obtained. In dealing with these returns it is to be noted that the systems of measurement, the methods of recording results, and the tabulation of the records are different in each country, and such figures are of little service unless reduced to some common standard of measurement.

TABLE I.[1]

SHOWING ANNUAL PRODUCTION OF WOOD PULP FOR VARIOUS COUNTRIES, CALCULATED ON THE AIR DRY BASIS (1907—1908).

Country.	Mechanical pulp. Air dry tons.	Chemical pulp. Air dry tons.	Total annual production.
Germany . .	315,000	320,000	635,000
Norway . .	421,000	270,000	691,000
Sweden . .	78,000	510,000	588,000
Finland . .	69,000	52,000	121,000
America . .	868,000	988,000	1,856,000
Canada . .	565,000	172,000	737,000
	2,316,000	2,312,000	4,628,000

The most convenient unit which may be taken as the basis of measurement for comparison is the "cord" of wood, consisting of a number of short logs, each 4 feet long, piled up in a space 8 feet long and 4 feet high. Such a pile of logs measuring 8 feet × 4 feet × 4 feet = 128 cubic feet, is called a "cord" of wood. The unit of weight may be taken in terms of the English ton of 2,240 lbs. (See p. 85.)

These figures do not convey even in such concrete

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[1] The sources of information from which Table I. has been compiled are as follows:—Germany: Figures given by Dr. Kirchner in "Wochenblatt," 1907. Scandinavia: Report British Wood Pulp Association, 1909. America: "Wood Used for Pulp," U.S.A. Bulletin. Canada: "Wood Pulp in Canada," official report, Geo. Johnston. Finland: *Paper Trade Review*, 1908.

form any accurate picture of the extensive cutting operations which are going on, for the manufacture of wood pulp. Some idea may possibly be obtained by attempting to estimate the number of standing trees felled to supply the quantity of pulp wood mentioned. This will vary in different countries according to the nature and size of the trees. According to general practice, the large trees are reserved for lumber and the manufacture of boards for building purposes, so that the trees used for pulp may be taken at an average diameter of about 9 inches.

The ordinary spruce or pine tree of this diameter will yield three logs, each 16 feet long, and when the logs are cut into 4-feet lengths, twelve pieces.

The number of pieces required to give a piled cord of 128 cubic feet capacity is about sixty, so that for each cord five trees would be necessary.

Assuming that 1 ton of dry chemical pulp is obtained from 2¼ cords of wood, and 1 ton of mechanical pulp from 1¼ cords of wood, then the total quantity of timber to be cut for the production of the amount of wood pulp shown in Table I. would be about eight million cords.

A certain proportion of the trees cut are faulty and decayed, while some are lost in transit from the forest to the pulp mill, so that the actual number felled for pulp wood is somewhat in excess of the quantity indicated. In relation to forestry and the destruction of forests, we have to consider, in addition to the wood cut for pulp, the number of trees required for timber, and the sum of these figures reaches formidable dimensions.

Forestry.—The available forest areas of different countries have been given by Schlich as follows :—

TABLE II.

Country.	Acres (millions).
Canada	800
America	400
Russia	500
Austria-Hungary	46
Germany	35
Sweden	49
Spain	21
Norway	17
France	23
Italy	10
Roumania	5
Great Britain	3

The preservation of the forests in wood-producing countries is thus an acute problem, and of recent years the subject of afforestation has aroused considerable interest in England, especially in regard to the industrial possibilities; but incidentally also as affecting rainfall, and therefore general agriculture. One of the most important questions, therefore, in this connection is the calculation of area necessary to supply a mill continously with wood pulp.

For example, What area of land planted with spruce and hard woods would be necessary to supply a mill having an output of 300 tons of newspaper per week?

This quantity of paper would require 200 tons of mechanical pulp and 100 tons of sulphite pulp per week, amounting to an annual supply on a basis of fifty weeks' work, of 10,000 tons mechanical pulp and 5,000 tons sulphite pulp.

Taking 1¼ cords of wood as the quantity required for 1 ton of mechanical pulp and 2¼ cords of wood for 1 ton dry sulphite pulp, the annual supply of wood necessary is 12,500 cords for mechanical, and 11,250 cords for sulphite pulp, or an approximate total of 25,000 cords.

The actual amount of spruce or pulp-producing woods per acre varies enormously in different countries and in different localities, and it is difficult to fix an average. In thickly wooded areas which have not been cut over, the quantity frequently reaches 40 to 50 cords per acre; but on timber lands which have been continuously "operated" the amount may not exceed 3 to 4 cords.

Taking 10 cords to the acre as a moderate and probable allowance, then in the above case 2,500 acres would be required to give the wood pulp necessary for one year. If the total forest area was 100,000 acres, then the timber available would be sufficient for forty years' supply. During that period the spruce largely reproduces itself, so that by progressive and careful management of the forest in the matter of planting and reproduction, an area of 100,000 acres should afford a perpetual supply to the mill quoted.

Mr. Parker Smith, in a paper entitled "Afforestation," read before the English Paper Makers' Association, 1910, says that at the Canadian Convention one manufacturer stated he could run his mill perpetually on a grant of 25,000 acres, which would permit of his cutting on a forty years' rotation, and yield, on a basis of 10 tons of pulp per acre, a total of 6,000 tons annually.

Comparing this statement with the one already quoted, and assuming that the 6,000 tons consisted of 4,000 tons mechanical pulp and 2,000 tons sulphite pulp, the weekly production of the mill works out at 120 tons of paper per week, requiring 10,000 cords of pulp wood. On this computation the manufacturer referred to was calculating the quantity of pulp wood per acre to be 16 cords.

Pinchot, the well-known American forestry expert, has carried out some valuable and elaborate experiments on the subject of the growth of spruce. A large area of forest land was carefully examined for the nature of the timber, its condition, growth, and other important information. Careful attention was given to the rate of the growth of the timber both in the virgin forest and also on areas which had been previously "operated" for timber. The data obtained in this investigation enabled Mr. Pinchot to construct tables showing the amount of timber which could be cut from the forest, and the number of years which would elapse before an equal quantity of timber could be cut from the same area. One example of this will be sufficient:—

A man owns 100,000 acres, yielding on an average 7 cords per acre of spruce 10 inches and over in diameter. How much can he cut annually if he wishes to obtain a sustained annual yield, and how soon can he return to the portion cut over the first year, and cut the same amount of timber about the same diameter limit as at first?

In the tables published by Mr. Pinchot the total amount of wood with a diameter limit of 10 inches appears to be 100,000 × 7 cords = 700,000 cords, while the same yield of pulp wood could be obtained after thirty-seven years. The area to be operated annually will be 100,000 ÷ 37, namely, 2,700 acres. The annual cut of wood will be

700,000 ÷ 37 = 19,000 cords. This illustration, taken at random from the experiments of Mr. Pinchot, coincides closely with the other cases quoted, and if the diameter limit was reduced to 9 inches a larger annual cut would have been obtained.

The problem of forestry has been studied and worked out on a successful commercial basis in several European countries. In Saxony, for example, the State control of an area of 430,000 acres has resulted in a large and profitable turnover, giving a steady revenue of increasing amount, as well as constant employment to skilled labour. In fifty years the State has realised the sum of £40,000,000, and the careful scientific methods of cutting, aided by proper attention to means for reproduction, has improved the quantity and quality of available timber. At a recent meeting of the Canadian Forestry Convention it was shown that the amount of standing timber in the State of Saxony had increased by 16 per cent., even during the period of constant cutting, and that the net revenue was 22*s.* as compared with 4*s.* fifty years previously.

The same satisfactory results are shown by other countries in which forestry as a commercial undertaking has been treated seriously.

In England the matter has been under consideration for some time, and the Report of the Committee on Re-afforestation, issued in 1909, is full of useful and suggestive evidence. It is interesting to note that the waterworks committees of several large municipal corporations, such as Liverpool, Manchester and Birmingham, have taken up the question, primarily for the purpose of conserving the rainfall incidental to the watershed under control, and then turning the large areas thus acquired for maintaining the water supply to useful account by planting trees.

The attractiveness of afforestation in the United Kingdom is clearly shown by the Committee's report. The conclusions arrived at are briefly—

1. Afforestation is a practicable scheme, the available area in the United Kingdom being 9,000,000 acres.

2. The best rotation to secure a continuous yield of wood requires 150,000 acres to be dealt with annually.

3. Afforestation is a productive investment for the development of the full scheme, for 9,000,000 acres would require an annual sum of £2,000,000. The net deficit would be £90,000 in the first year, rising progressively to £3,131,250 in the fortieth year, in which period the forest becomes more than self-supporting.

4. After eighty years the net revenue at present prices for timber should be £17,500,000. This represents 3¾ per cent. on the net cost calculated at accumulating compound interest at 3 per cent.

5. Afforestation creates a new industry which does not compete with private enterprise, and would afford permanent employment to one man per hundred acres, and temporary employment to a large number of men during the winter months.

Cost of Afforestation.—The Committee gives the following example :—

We assume, as regards expenses, that :—

1. 150,000 acres are annually afforested for sixty years, and that the cost of the freehold and expenses of afforestation amount to £13 6*s.* 8*d.* per acre.

2. The annual outlay for administrative expenses is 4*s.* per acre.

3. One-third of the area is worked on a forty years' rotation, and two-thirds on an eighty years' rotation.

4. The cost of re-afforestation is £6 10*s.* per acre; and

5. The rate of interest is 3 per cent. per annum.

We further assume, as regards receipts, that—

1. Thinnings take place at the end of the twentieth year, and at the end of each successive decade from the date of planting.

2. The net receipts for the initial thinnings amount to 2*s.* 6*d.* per acre, and for the succeeding thinnings are at the rate of £3, £6, £9, £12, and £15 per acre respectively.

3. The area which is afforested on an eighty years' rotation yields £175 per acre on being clear-felled at the end of eighty years.

4. The area which is afforested on a forty years' rotation yields £60 per acre on being clear-felled at the end of forty years; and

5. The rate of interest is 3 per cent. per annum.

The annual deficit on the transaction rises from £90,000 in the first to £3,131,250 in the fortieth year; in the forty-first and up to the sixtieth year the forest becomes practically self-supporting; in the sixty-first year, and subsequently, an increased revenue is received, but it is not until the eighty-first year that the full results are obtained; in this year and subsequently an approximate equalised revenue of £17,411,000 per annum being realised. Further calculations show that the value of the property would then be £562,075,000, or £106,993,000 over and above the cost of its creation. The equalised annual revenue of £17,411,000 represents a yield of £3 16*s.* 6*d.* (approximately) per cent. on the excess of accumulated charges over receipts.

Measurement of Pulp Wood.—The systems for measuring wood used in the manufacture of pulp differ in the several countries.

Scandinavia.—The wood is measured in terms of fathoms or of cubic metres, the price paid for raw material being determined by reference to a table showing the sum to be paid for logs of varying lengths and varying diameters.

One fathom = 6 feet.
One cubic fathom = 216 cubic feet.

Germany.—Wood is usually measured in Germany and other Continental countries by the cubic metre. A cubic metre of piled logs is called a Raummeter, the amount of actual solid wood contained in the pile being known as a Festmeter, the relation between these measurements being

One Raummeter = 0·77 Festmeter.
One cubic metre = 35·314 cubic feet.

America.—Many systems are in use, the most common being the measurement by *cords.* A cord is a pile of logs 8 feet long, 4 feet wide and 4 feet high.

One cord piled logs = 128 cubic feet.

Canada.—Measurements are also based upon the use of a *cord* of wood, in two ways, the first being the *piled cord* of 128 cubic feet and the second a *solid cord* which is the amount of solid wood contained in a piled cord, the relations being as follows :

One piled cord = 128 cubic feet in the whole pile.
One solid cord = 115 cubic feet of solid wood.

This measurement of a *solid* cord has been established by the government of the province of Ontario, and was arrived at by means of a large number of special experiments carried out for the purpose of establishing a common standard of measurement. It does not represent accurately the total amount of solid wood in an ordinary cord of 128 cubic feet, but it is a figure which has been selected as the standard for the payment of dues.

In the province of Quebec a cord of pulp wood is considered equal to 600 feet board measure, which relation was determined by a series of elaborate tests instituted for finding the amount of useful timber obtained from logs intended for lumber. This relation is used as a basis for calculating payments due to government, and does not necessarily represent the true equivalent, which varies according to the size of the log.

The true measurement of the amount of wood in the logs is best secured by determining the actual cubical contents of each log separately. By this means all errors due to methods of piling the logs in stacks or to the varying lengths of the logs, is easily avoided.

The importance of this question is easily shown in the following test made by an expert.

Forty-two logs, each 16 feet long, were piled up carefully in a rack, the measurement of the wood being exactly three piled cords or 384 cubic feet. The 16 feet logs, after being measured and piled, were cut in half and again piled. The stack was measured and then the logs were again halved, giving pieces 4 feet long, which were stacked up and measured. Finally the pieces were reduced to a length of 2 feet, and the process of stacking and measuring repeated. The results are set out in Table I.

TABLE I.

No. of pieces.	Length, feet.	Dimensions of pile.	No. of piled cords.	Ratio.
42	16	16 × 16 × 4	3·00	100
84	8	1 × 6 × 7·5	2·81	93·7
168	4	4 × 12 × 7·16	2·69	89·7
336	2	2 × 12 × 13·83	2·59	86·3

The effect of the closer packing rendered possible by the reduction of length in the log is plainly shown in this table. Thus 100 piled cords of wood measured in 16 feet lengths only measured 89·7 when reduced to 4 feet. The latter is a customary unit of measurement for pulp wood. Even in the case of wood cut in 8 feet or 4 feet lengths there would be a difference of four cords in the measurement, according to the length into which the logs are cut. This figure will naturally vary with different logs, and cannot be accepted as being applicable to all kinds of wood whether of large or small diameter.

The practical effect is also shown in Table II.

TABLE II.

Length of pieces. Feet.	Piled cords obtained from 100 solid cords.	No. of pieces required to give piled cord.	Weight of a piled cord. lbs.	Extra 16 ft. logs required to give the piled cord of stated lengths.	No. of cubic feet in piled cord.
16	137	14	3,355	0	84·3
8	128	30	3,580	1	90·0
4	122	61	3,740	1¼	94·0
2	118	129	3,880	2	97·0

This table is interesting as showing the exact result, in a practical manner, of reducing the length of the log, the difference being shown not only in the weight of the wood, but also in the very concrete fact that an extra log or two is required to make up the reduction.

TABLE OF EQUIVALENTS.

	Cubic fathoms.	Cubic feet.	Cubic metres.	Cords.
One cubic fathom is	—	216	6·113	1·0687
One cubic foot is .	0·00463	—	0·283	0·00781
One cubic metre is	0·163	35·314	—	0·276
One cord is . .	0·5926	128	3·6224	—

WOOD PULP TREES.

The chief woods used for the manufacture of pulp are the species of spruce, fir and pines for sulphite and mechanical pulps, the aspen, poplar and other deciduous trees for soda pulps. The conifers are also used for the manufacture of soda and sulphate pulps. For wrappers and fibre papers, hemlock is used in considerable quantity.

The following is an alphabetical list of common woods, many of which, however, find no place at present in the wood pulp industry. These are printed in italics in the name column.

Common name.	Botanical name.	German.	Specific gravity.	Weight of cubic foot in lbs.
Acacia	Robinia pseudacacia	Schotendorn	·73	45·7
Alder	Alnus glutinosa	Gemeine-erle (Roth-erle)	·46	29·0
Ash	Fraxinus excelsior	Weiss-esche	·65	40·8
,, *Mountain Ash*	Pyrus aucuparia	Eber-esche	·54	34·0
Aspen	Populus tremula	Zitter-pappel (Aspenholz)	·50	31·3
Balsam	Abies Fraseri		·36	22·2
Basswood	Tilia Americana	Linde	·45	28·2
Beech	Fagus silvatica	Rotbuche	·75	46·8
Birch	Betula alba	Birken-holz	·64	40·0
Chestnut	Castanea sativa	Kastanje	·45	28·1
Cottonwood	Populus monilifera	Wollpappel	·39	24·2
Crack Willow	Salix fragilis	Bruchweide	·45	28·3
Cypress	Taxidium distichum	Cypresse	·45	28·3
Elm	Ulmus campestris	Steinlinde (Roth-rüster)	·69	43·3
Fir	Picea excelsa	Fichte. Föhre	·49	30·0
,, Silver Fir (India)	Abies pindrow	Tannenholz-Tanne	·46	29·0
,, Silver Fir (Europe)	Abies pectinata	Tannelholz-Tanne	·49	30·0
Hemlock	Abies canadiensis	Schierlingstanne	·42	26·4
Hornbeam	Carpinus betulus	Weissbuche (Hagebuche)	·72	45·0
Larch	Larix Europea	Lorche	·74	46·1
Maple	Acer dasycarpum	Ahorn	·52	32·8
Paper Birch	Betula papyrifera		·60	37·1
Pines		Kiefer. Nadelholz		
Black Pine	Pinus austriaca	Schwarzföhre	·57	35·4
White Pine	Pinus strobus	Wehmuthskiefer	·38	24·0
Pitch Pine	Pinus palustris	Gelbkiefer	·70	43·6
Poplar	Populus	Pappel	·40	25·6
White Poplar	Populus alba	Silberpappel	·48	30·0
Black Poplar	Populus nigra	Schwarzpappel	·48	30·0
Sallow (*Willow*)	Salix capræa	Sahlweide	·55	35·0
Sandalwood	Santalum album	Santalholz	·98	60·0
Spruce	Picea excelsa	Fichte (Tanne)	·42	26·7
White Spruce	Picea alba	Weisstanne	·40	25·2
Tamarac	Larix americana	Lorche	·62	38·9
Willow	Salix nigra	Weide	·44	27·7

Coniferæ. Cone-bearing trees . . . . Nadelholz.
Deciduous or leaf-bearing trees . . . . Laubholz.

The History of Mechanical Wood Pulp.—The possibility of using wood for papermaking seems to have been deduced from the Réaumur observation that wasps build their nests from partially decayed wood which they obtained from trees or timber. In 1765 J. C. Schaffer, a priest in Regensburg, published a book containing samples of paper made from many raw materials, and referring especially to wood, wrote: "it must be possible, though with different methods, to make paperstuff from wood and consequently use it instead of the ordinary rags for papermaking."

This is an interesting statement in view of the fact that nothing was then known of the use of alkalies or other chemical agents for reducing fibrous materials to pulp.

Schaffer experimented with the material of the wasps' nest, with sawdust and shavings. From some seven or eight species of wood he made excellent sheets of paper, having regard to the means at his disposal. He published a second edition of his book, entitled, "Sämtliche Papierversuche-Nebst 81 Mustern und 13 Kupfertafeln," in 1772, and enlisted the services of a papermaker, Meckenhauser, to enable him to produce some better results.

In 1800 Matthias Koops, a Dutchman, published a book which he printed on paper made from straw pulp and dedicated to King George III. He added an appendix to his work which was printed on paper made entirely of wood pulp, an idea suggested to him no doubt by the work of J. C. Schaffer. Koops was a man of some enterprise, for he also issued a work on paper made entirely from old waste paper, this being probably the first attempt to utilise old waste material for such a purpose.

In 1840 Friedrich G. Keller, a young weaver of Haynich, in Saxony, reading in a scientific journal of the great scarcity of rags as material for papermaking, resolved to keep his eyes open for a substitute. In 1843 his attention was called to the remarkable paperlike appearance of the wasps' nest, and recollecting that in his school days he had ground down cherry stones on an ordinary grindstone in order to make a cherry chain, he tried the effect of holding a piece of wood against the revolving stone. To his great delight the experiment was successful, and he collected the fibres so isolated from the wood and made a minute piece of paper.

Keller continued his experiments, and in 1844 manufactured about 2 to 3 cwt. of pulp, which was beaten up with rag pulp and made into paper. In 1845 he parted with the secret of his process, and disposed of it to Heinrich Volter for the sum of 700 thaler (£140) !

The progress of the new method was somewhat slow, but improvements, including the necessary treatment for refining the pulp, or removing the coarse chips, were introduced, and towards 1860 the process was put on a more satisfactory footing. In 1862 Volter was awarded the medal of the International Arts and Industries Exhibition in London.

Between 1862 and 1865 seven or eight pulp mills were erected in Germany and Scandinavia and the manufacture of ground wood pulp on a large scale became an accomplished fact.

History of Chemical Wood Pulp.—The early attempts of Koops in 1800 to utilise straw, and his few experiments with wood as substitutes for rag, may be regarded as the starting point in the history of chemical wood pulp. The materials were probably boiled with some crude soda ley and subsequently beaten into pulp. About this period soda ash, caustic soda, chlorine and bleaching powder and other chemicals had been introduced to the manufacturing world, so that the possibilities for reducing vegetable products to the condition of pulp were much greater.

In 1857 Houghton patented a process for digesting wood with caustic soda at high temperatures in closed vessels.

In 1863, Tilghmann, an American chemist, suggested the use of a solution of sulphurous acid gas. His early experiments were carried out in lead-lined vessels, but the work was abandoned owing to difficulties connected with the construction of suitable digestors.

As Tilghmann was the inventor of a process which has become the basis of a large and important industry, the following *précis* of his first patent, as given by Mr. A. D. Little, may be quoted as having a peculiar interest :—

> The process of treating vegetable substances which contain fibres with a solution of sulphurous acid in water, either with or without the addition of sulphites or other salts of equivalent chemical properties as above explained, heated in a closed vessel, under pressure, to a temperature sufficient to cause it to dissolve the intercellular incrusting or cementing constituents of said vegetable substances, so as to leave the undissolved produce in a fibrous state, suitable for the manufacture of paper, paper pulp, cellulose, or fibres, or for other purposes, according to the nature of the material employed.
>
> I also claim as new articles of manufacture the two products obtained by treating vegetable substances which contain fibres with a solution of sulphurous acid in water, either with or without the addition of sulphites or other salts of equivalent chemical properties, as above explained, heated in a closed vessel, under pressure, to a temperature sufficient to cause it to dissolve the intercellular or incrusting constituents of said vegetable substances, one of said products being soluble in water, and containing the elements of the starchy, gummy, and saline constituents of the plants, and the other product being an insoluble fibrous material, applicable to the

manufacture of paper, cellulose or fibres, or to other purposes, according to the nature of the material employed.

I also claim the use and application, in the manufacture of paper, paper pulp, cellulose and fibres, of the fibrous material produced by treating vegetable substances which contain fibres with a solution of sulphurous acid in water, either with or without the addition of sulphites or other salts, of equivalent chemical properties as above explained, heated in a closed vessel, under pressure, to a temperature sufficient to cause it to dissolve the incrusting or intercellular constituents of said vegetable substances.

I also claim the use and application of sulphites or other salts of equivalent chemical properties as above explained, in combination with a solution of sulphurous acid in water, as an agent in treating vegetable substances which contain fibres, when heated therewith in a close vessel, under pressure, to a temperature sufficient to cause the said acid solution to dissolve the intercellular or incrusting constituents of said vegetable substances.

I also claim the recovery and re-use of sulphurous acid and sulphite from the acid liquids which have been digested on the vegetable fibrous substances, by boiling said liquids or neutralising them with hydrate of lime.

In 1872 Ekman had developed a process which was commercially successful, and this was introduced into England, at Ilford, Essex, about 1884, a mill being erected a few years later at Northfleet in Kent for the treatment of wood by means of bi-sulphite of magnesia.

In 1876, Mitscherlich, a celebrated German chemist, experimented with sulphurous acid and devised a method for converting wood into pulp by cooking under low pressure for a long period, producing a half-stuff eminently suitable for certain classes of paper.

Numerous and extensive modifications of the original Tilghmann sulphite process have resulted in the evolution of an industry typical of modern chemical engineering. Such modifications refer to details of working, more particularly to the type of boiler or digestor, to economy in the amount of sulphur used, to improving or varying the quality of the pulp, and to general efficiency, and are of subordinate historical interest.

There has been a good deal of controversy as to the priority of original invention of this most important industrial development. It has always appeared to us that while Tilghmann is the pioneer from the technological standpoint, on the clear and specific claims of his patent above set forth, the practical and industrial pioneers were George Fry and his collaborator Ekman. Some years in advance of the bi-sulphite process (1869) Fry investigated the action of water only at high temperatures and pressures, paying particular attention to the volatile by-products of the complex reactions; and in this investigation secured the collaboration of the late Greville Williams, who identified furfural amongst the products of decomposition of the ligno-cellulose.

Finding that the resolution of the wood under these conditions was limited by the influences of oxidation and condensation, it was then suggested by Fry to Ekman, who had become associated with these researches, to seek for a new chemical condition to antagonise these influences. In this path of logical though empirical evolution this group of pioneers may be held to have independently discovered the bi-sulphite process; and Ekman, with George Fry, had the satisfaction of working the process to an industrial and commercial success at Bergvik, Sweden, then at Ilford, and lastly at Northfleet.

The following is a chronological list of inventions for the preparation of pulp from wood by chemical reactions:—

Year.	Name.	Process.
1840	Payen	Nitric Acid
1852	Coupier & Mellier	Soda
1853	Watt & Burgess	Alkalis
1855	Jullion	Alkaline salts
1857	Houghton	Alkalis
1861	Barre & Blondel	Dilute acids
1864	Bachet & Machard	Acids
1866	Tilghmann	Sulphurous Acid and salts
1867	Fry	Water at high temperatures
1870	Ekman	Magnesium Sulphite
1870	Dresel	Soda
1871	R. Mitscherlich	Sulphurous Acid and salts
1872	Ungerer	Soda
1872	Rotter-Kellner	Sulphurous Acid and salts
1880	Cross	Water and neutral sulphites
1881	Francke	Sulphurous Acid and salts
1882	Pictet & Brelay	Sulphurous Acid
1882	Graham	Sulphurous Acid and salts
1883	Blitz	Alkalis and sulphites
1883	Dahl	Sulphates and sulphides
1885	Kellner	Electrolytic process
1890	Lifschutz	Nitric and sulphuric acids
1894	Cross	Nitric Acid—dilute

CHAPTER IV

THE MANUFACTURE OF MECHANICAL WOOD PULP

The term "mechanical" or "ground" wood pulp is applied to pulp which has been prepared by a mechanical process. The principle of the operation is merely the disintegration of wood into fibres by means of a grindstone, the wood being brought into contact with the stone as it revolves. The conditions of manufacture are capable of considerable modification so that various grades and qualities of product are possible.

Preparation of Wood.—The logs of wood, which have been brought to the mill from the timber limits or other sources, and which vary in length from 10 to 16 feet, are first reduced to a uniform length of 24 inches by means of large circular saws.

The arrangements in a modern pulp mill for handling the logs and preparing them for conversion into pulp call for considerable skill and attention in order to produce the optimum result at minimum cost.

The short pieces of wood are automatically conveyed to the "barking" room and there deprived of the outer bark. The machine used for this purpose consists of a heavy circular iron disc enclosed in a strong casing. The disc is provided with three knives projecting from the surface of the disc in such a manner that when the short pieces of wood are pressed against the surface of the disc, as it revolves, they are completely denuded of the bark itself. A considerable proportion of wood is lost in this process, the amount varying from 15 to 25 per cent., according to the size and condition of the logs. The bark is generally burnt in special ovens and utilised as fuel.

The clean pieces of wood may be employed for the manufacture of either mechanical or chemical wood pulp and in practice the pieces are often sorted out, the clean wood free from dirt and knots being reserved for chemical pulp, and the inferior wood being converted into mechanical wood pulp.

Cold-ground Pulp.—When the wood is ground into fibres in the presence of a large excess of water, a fine even pulp of uniform quality is produced. This pulp is known as "cold-ground" in contradistinction to "hot-ground" pulp, which is produced under the condition of high temperature (*infra*).

The machine used for the manufacture of the cold ground pulp consists of a horizontal grindstone, usually 60 inches in diameter and with 27 inches breadth of face, mounted on a heavy vertical shaft and encased in a strong cast-iron circular box, as shown in Fig. 14. Around the circumference of the box there are a number of recesses or "pockets" in which the short 2 feet pieces of wood are placed. The wood is pressed against the surface of the rotating grindstone by pistons operating under hydraulic pressure, water being continuously applied to the surface of the stone so that the disintegrated fibres are carried away from the stone into storage reservoirs for subsequent treatment.

Hot-ground Pulp.—When the quantity of water flowing to the grindstone is reduced to a minimum then the temperature of the mass in contact with the stone rises rapidly on account of the friction, and the wood is thus ground to pulp

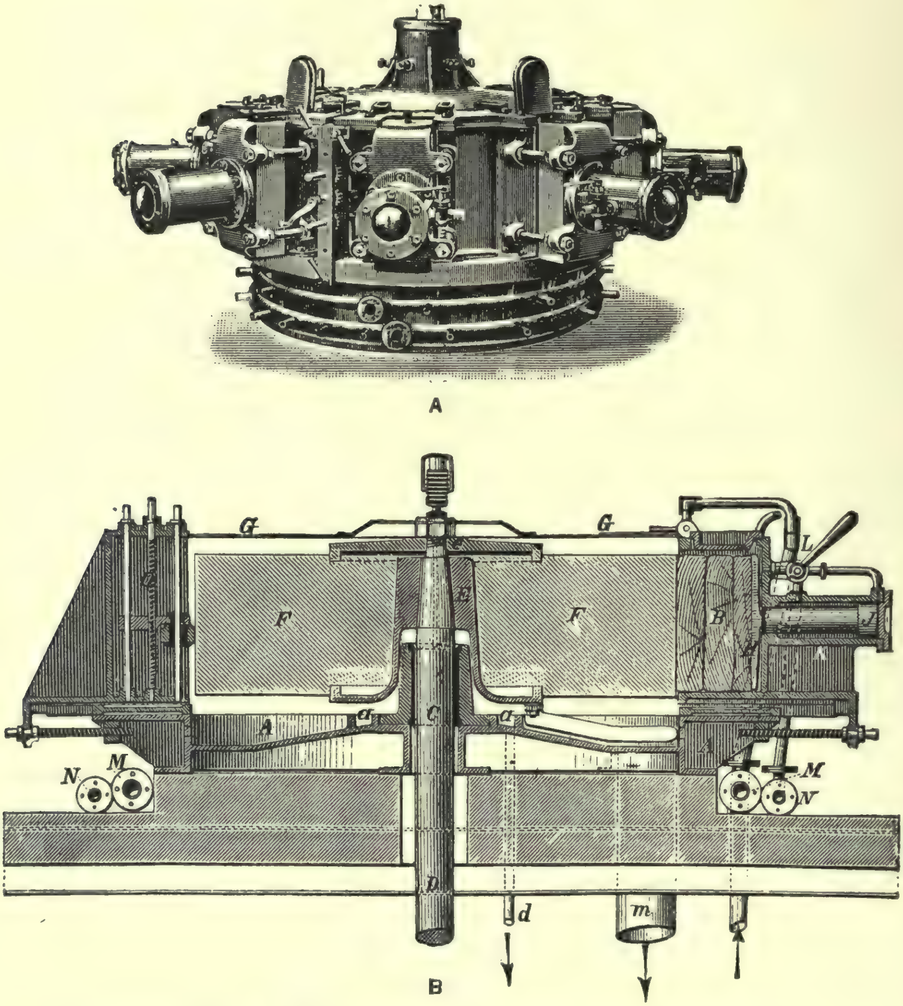

FIG. 14.—View of Horizontal Grinder (A), with Section (B).

under entirely different conditions. The fibres are readily torn away from the wood, and produce a pulp which is much coarser than the cold-ground pulp, the fibres being longer.

The machine used for the manufacture of this pulp consists of a grindstone mounted in a vertical position on a horizontal shaft, operated by a water turbine. The stone is enclosed in a circular iron casing provided with "pockets" into which the blocks of wood are placed. The pieces of wood are forced against the surface of the stone by hydraulic pressure.

The water is supplied to the grindstone in limited quantity, just sufficient being used to prevent the pulp from being burnt or spoilt. The temperature frequently rises to 150° Fahr., owing partly to the greater pressure of the wood against the stone, and also by the conditions under which a limited supply of water is used. Pulp of this kind works freely on a fast-running news machine—that is, as the pulp and water flow on to the wire of the paper machine the water drains quickly and freely through the meshes of the wire, and thus makes it possible for the machine to be operated at a high speed. Many of the paper machines used for the manufacture of "news" with pulp of this character can be run at a speed of 500 to 600 feet per minute.

The quantity and quality of the pulp produced as controlled by the conditions of grinding depend on

(1) The sharpness of the stones;
(2) The pressure applied to the blocks of wood;
(3) The temperature of the mass;
(4) The method of applying the wood to the stone.

In general terms, the quantity of the pulp is increased by the use of sharp stones and the application of pressure, the yield being highest with wood treated by the hot-ground process.

The coarseness of mechanical wood pulp is merely a relative term, for it is possible to have a badly-ground wood pulp well screened, giving a coarse material of an even uniform grade, or, on the other hand, a well-ground wood badly screened giving a high-class pulp, spoilt by the presence of long chips or slivers which have not been removed. Such slivers in pulp are a fruitful source of "breaks" on the paper machine, since they locally reduce the tensile strength of the web. Coarse pulp of a uniform grade does not produce "breaks," but the fibres do not lie closely in the surface of the paper, with the result that a large quantity of "fluff" is produced on the type of the rotary printing presses.

The output of a grinder is increased by sharpening the stone and by increasing the pressure applied to the blocks of wood. The effect of using sharp stones is clearly indicated by the following experimental results, obtained from two or three pulp mills :—

Mill.	Pounds of wood treated per hour.		Ratios.	
	Dull stones.	Sharp stones.	Dull stones.	Sharp stones.
A	440	680	100	155
B	637	1064	100	167
C	628	830	100	138

The amount of wood pulp obtained from a grinder depends chiefly upon the pressure applied to the wood in contact with the stone, as shown by Kirchner's elaborate experiments tabulated in the following table :—

Pressure on stone. Lbs. per sq. in.	Consumption of power. H.P.	Yield of air-dry pulp per hour. Lbs.	H.P. required for 24 hours for 1 ton air-dry pulp.
1	1·15	1·25	86·0
2	1·95	3·30	56·8
3	2·60	5·15	47·0
4	3·15	6·60	44·5
5	3·80	7·92	44·7
5·5	4·05	8·05	44·4
6	4·40	8·30	49·4
7	5·0	7·92	59·0

The effective work of the stone under the conditions of the experiment is evidently reached when the pressure is 5·5 lbs. per square inch, for at this point the power required for a given output is lowest.

Kirchner gives the following interesting table showing the influence of the condition of the stones on various kinds of wood:—

PRODUCTION OF PULP PER H.P. PER 24 HOURS UNDER DEFINITE EXPERIMENTAL CONDITIONS.

Wood.	Well sharpened stones Lbs. of pulp.	Moderately sharpened stones. Lbs. of pulp.
Pine	6·4	5·4
Fir	6·8	—
Aspen	8·9	6·3
Poplar . . .	6·1	5·6
Lime	5·9	5·4
Birch	6·7	—
Willow . . .	7·2	4·6
Alder	—	6·3
Oak	—	5·1

In a more complete series of trials Kirchner studied the relation between the power consumed with stones of varying degrees of sharpness in producing a stated quantity of pulp and the pressure on the surface of the stone. These trials were conducted with the hot-grinding process, and the amount of pulp produced per twenty-four hours was taken as 100 kilos (say 220 lbs., or nearly 2 cwt.), the stones being worked under conditions giving this output. Three stones —fine, medium and coarse grades—were selected for the experiment. The general results obtained show that as the pressure increased, the power required decreased up to a certain point, when any further pressure at once created a demand for greater power. This is admirably shown in the diagram Fig. 15, where the experiments with the three classes of stone are shown by the curves, A, fine; B, medium; C, coarse.

The maximum output was obtained under the following conditions:—

Stone.	Pressure. Lbs. per sq. in.	Horse-power.	Output in 24 hours.
A. Fine . .	4·2	4	220 lbs.
B. Medium . .	12·6	2·4	220 lbs.
C. Coarse . .	8·4	2	220 lbs.

Excess of pressure is shown by the sudden upward turn of the curves, though with the coarse stone this point has not been reached.

The immersion of the lower half of the stone in water had a remarkable effect on the results.

The pressure can be increased enormously with a corresponding greater efficiency in the work of the stone, although

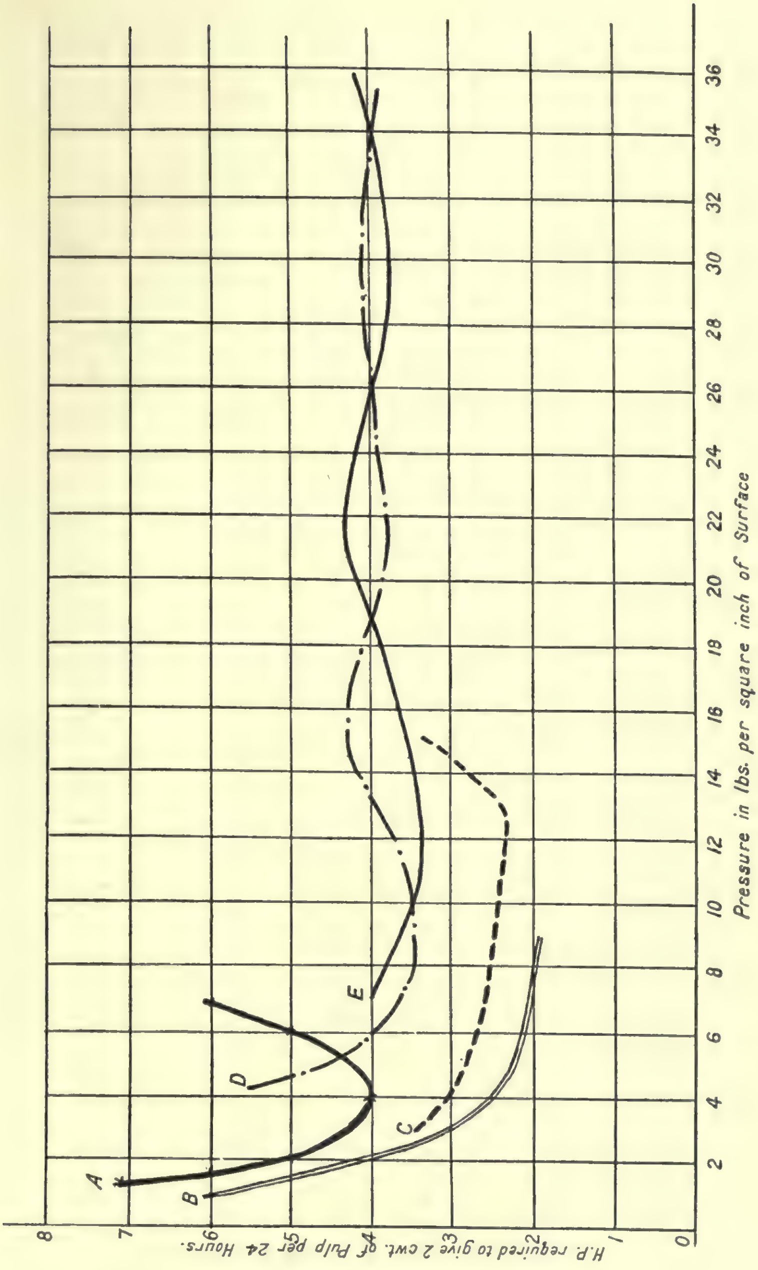

FIG. 15.—Curve for illustrating Power Trials.

the power required does not vary much. This is shown by the curve D, which after a pressure of about 8 lbs. to the square inch assumes a horizontal position.

Kirchner found that the output per unit of area of the total grinding surface was almost proportional to the pressure.

The diagram in Fig. 15 represents the results of some of the more important tests.

Curve A.—With a pressure of 1½ lbs. per square inch a stone with fine surface required, in twenty-four hours, 7⅓ h.p., and with a pressure of 3 lbs. per square inch, 4½ h.p. The greatest production was obtained when the pressure reached 4½ lbs. per square inch, when the power required to treat 2 cwt. of wood amounted to 4 h.p.

Curve B.—This curve represents the work of an average stone which required 3 h.p. under a pressure of 4½ lbs. per square inch. The power under a higher pressure of 14 lbs. per square inch was only 2½ h.p. for the same production.

Curve C represents the work of a coarse stone, the amount of power for a given production being reduced by the increase of pressure down to a certain point, after which any further increase of pressure required a greater amount of power. This is shown by the sudden rise of the curve when the pressure reached 13 lbs. per square inch.

Kirchner in his interesting experiments pointed out that these tests show the relation between the production of pulp with different kinds of stone at different pressures, and shows that for a maximum output under economical conditions it is important to choose the right pressure for a given stone. In a further series of experiments he kept the stone partially immersed in a mixture of pulp and water. The results are shown in curves D and E.

Curve D.—With a pressure of 4½ lbs. per square inch the power required for the production of 2 cwt. of pulp per twenty-four hours was 5½ h.p. The gradual increase of pressure was accompanied by a reduction in the amount of power required, and with a pressure of 15 lbs. per square inch the power was reduced to 4 h.p. The practical effect of the greatly increased pressure was seen in the finer condition of the pulp.

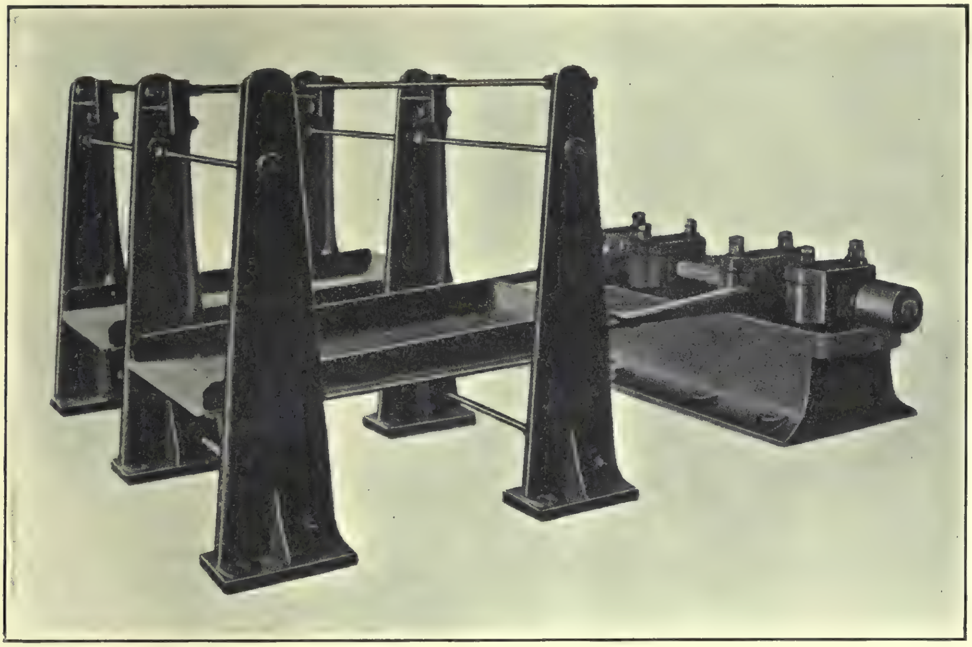

FIG. 16.—Shaking Screen.

Screening.—The pulp from the grinders is carefully screened to remove all chips and insufficiently ground pulp. Many forms of apparatus are employed, but all are based upon the same principle, the use of plates perforated with fine slits or circular holes allowing all the finer pulp to pass through, but retaining all coarse pieces.

The *shaking screen* shown in Fig. 16 consists of a horizontal shallow tray perforated with fine slits. The pulp, mixed with large quantities of water, flows on to the tray, which is kept in a violent state of agitation, and the fine pulp together with the water falls through the slits, while the coarse stuff is gradually forced along the surface of the tray and eventually falls over the edge into a trough of water or a travelling band conveyor.

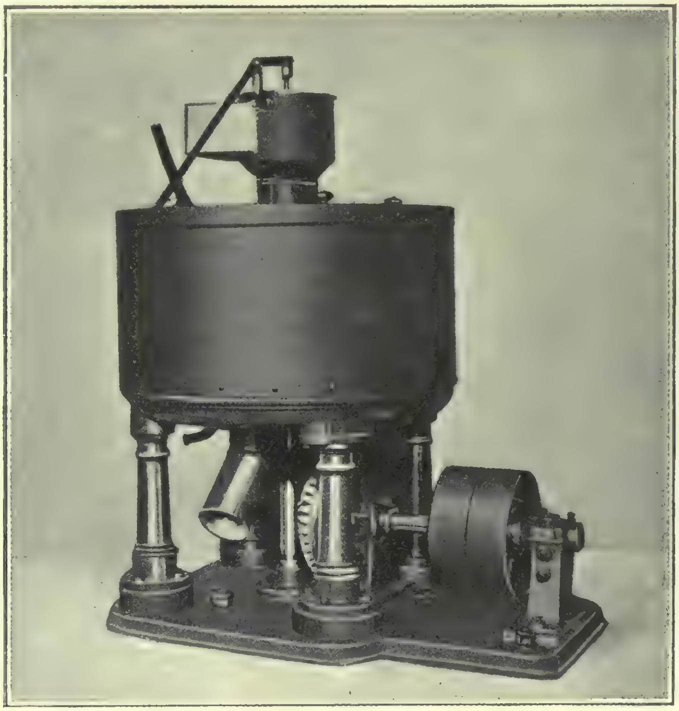

FIG. 17A.—Centrifugal Screen for Wood Pulp.

A flat screen is worked on a somewhat similar principle, but the motion of the plate is due to a violent agitation produced in a vertical direction instead of being to and fro in the horizontal direction. This produces a partial suction.

The *centrifugal screen*, Fig. 17A, the latest form of apparatus for separating out the coarse pulp, is a round vessel, containing a circular screen built up of perforated plates, which rotates at a high rate of speed, the fine pulp being forced through the slits by centrifugal force.

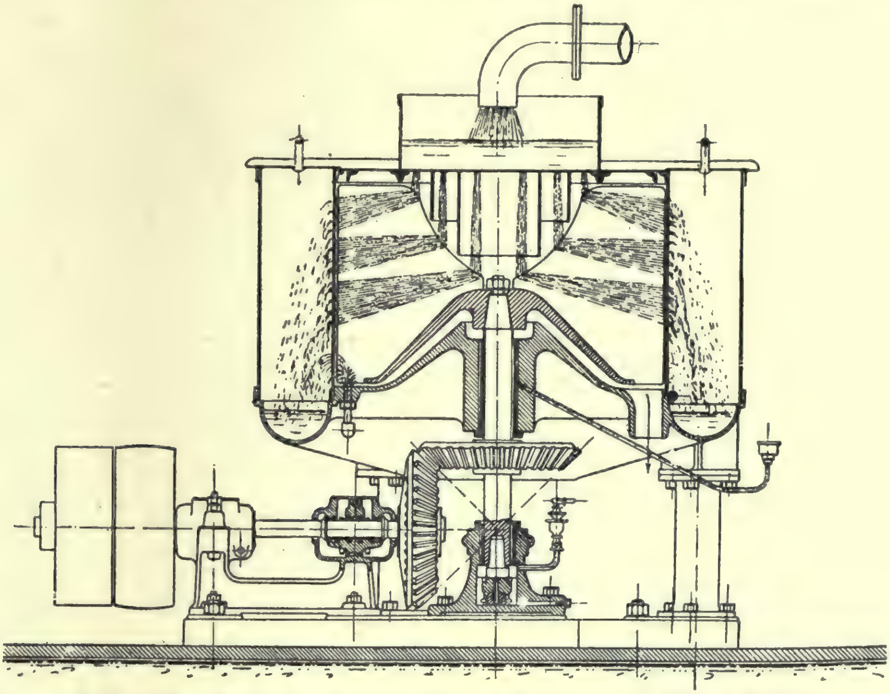

FIG. 17B.—Section of Centrifugal Screen for Wood Pulp.

The capacity of a screen is usually expressed in terms of the weight of dry pulp obtained in a given period. Such figures are not of much value without details as to the size and number of the perforations per square foot of area, as the capacity is readily increased by the simple process of enlarging the slits or holes.

Removal of Water.—When the pulp has been properly screened, it is treated in a wet press machine in order to remove the large quantity of water with which it is mixed, and to produce a pulp fit for shipment to the paper mill.

The dilute mixture is pumped continuously into a large vat in which rotates a hollow drum the surface of which is made of fine wire gauze. The pulp adheres to the drum, while the water is forced through the wire cloth and flows away into a trough fixed outside the vat. The thin skin of pulp is carried up above the surface of the water in the vat and is picked off by a travelling felt passing over a roller which is in contact with the drum. The thin sheet passes between small rollers, which squeeze out more water, and is then wound up in a continuous roll on a large wooden drum until it forms a thick sheet. This is removed at intervals either by hand or automatically.

In the most approved form of wet press machine the thick sheet is cut off at regular intervals by a knife which falls automatically. The sheet of pulp is therefore always of uniform thickness and weight, provided reasonable care has been exercised in keeping the ratio of water and pulp fairly constant. From the wet press machine the pulp is obtained in the form of thick sheets containing about 75 per cent. of water.

The sheets of pulp are finally submitted to pressure in powerful hydraulic presses which remove a further quantity of water and give a product containing 50 per cent. of air-dry pulp and 50 per cent. of water. These sheets are packed in bales of 4 cwt. and 2 cwt. capacity, and then fastened up with stout iron wire and wooden battens.

BROWN WOOD PULP.

In 1862 Lyman patented a process for submitting wood to the action of water at a high temperature, 160° C. In 1870 Meyh found that when wood previously digested in this way was mechanically treated in the grinder it gave a tough long-fibred stock. Since that date large quantities of brown wood pulp have been produced for the manufacture of box boards. The wood is either simply steamed, in which case a dark brown product is obtained, or digested in water at high pressure when a lighter coloured paper is produced.

Steamed Wood.—Logs of wood 12 or 16 feet long, or cut up in 2 feet lengths ready for the grinder, are packed into tall cylindrical boilers and steamed for twelve to thirty hours at a temperature varying from 120° to 160° C., the shorter period requiring a higher pressure. The water of condensation containing organic acids and volatile compounds such as acetic and formic acids, ethereal oils, turpentine and resin is drawn off continuously, or at intervals. In modern practice such by-products are carefully preserved and refined, having considerable value.

Wood Digested in Water.—A finer material of superior colour is produced when the wood is digested for twenty-four to thirty hours at a somewhat lower temperature in the presence of water, 60 lbs. pressure being the general practice.

The boilers are usually cylindrical in shape, and of considerable length, erected in a horizontal or vertical position. Cast iron is regarded as more suitable, being less liable to oxidation and corrosion from the organic

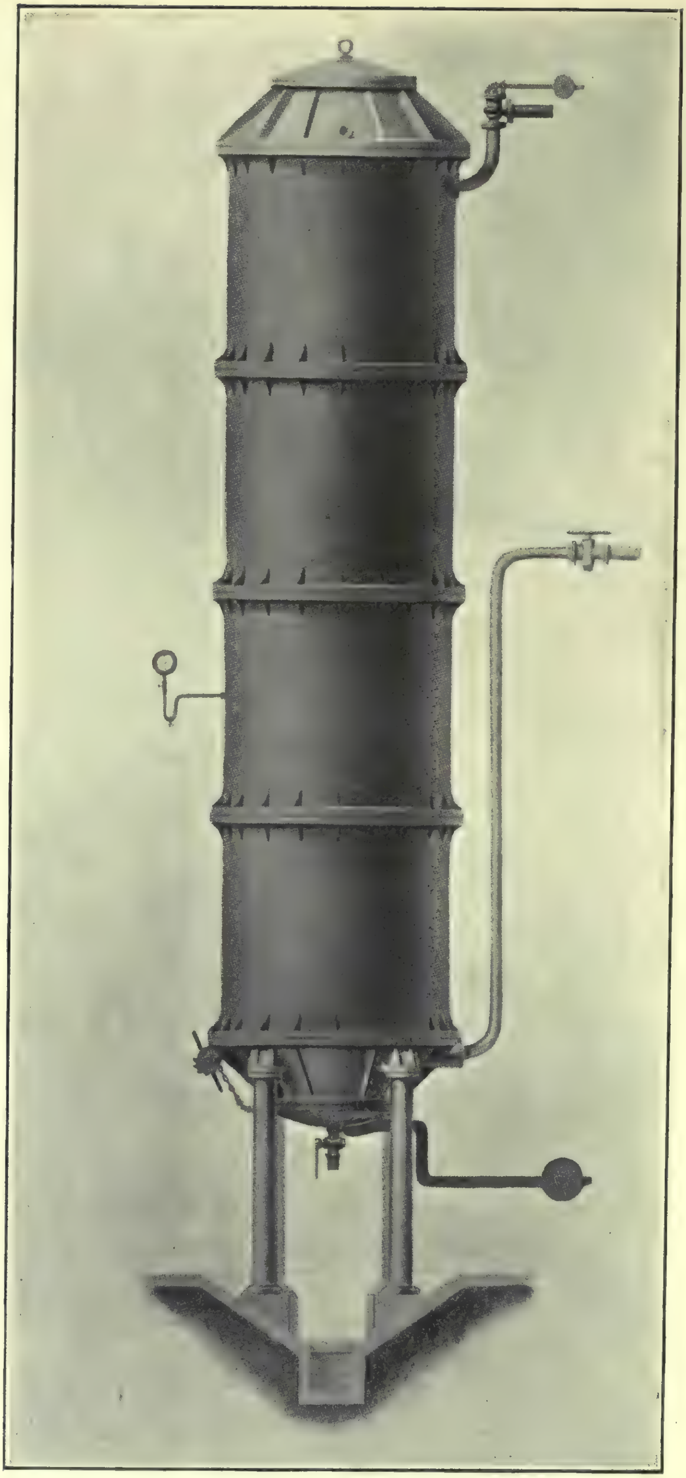

FIG. 18.—Digestor for manufacture of Brown Pulp.

acids produced during the operation. In Germany the practice obtains of lining the vessels with copper, and in one or two special cases digestors made of copper entirely have been built. The price of a wrought-iron copper-lined digestor 5 feet diameter and 17 feet long is about £192, while a digestor constructed entirely of copper of about the same capacity would cost £450.

Use of Brown Pulp.—Wood boiled in this way previous to grinding gives a material suitable for the manufacture of so-called " leather board " used for box making. It is exceedingly tough and flexible, can be bent to almost any shape without cracking or splitting, and when made up into boxes is capable of resisting great pressure. It is also used for the manufacture of imitation kraft paper and for common paper pattern tissues.

The Estimation of Mechanical Wood Pulp in Papers.

The determination of the exact percentage of mechanical wood pulp in papers is obviously a matter of importance. Considerable attention has been given to this subject of recent years, and the various available methods may be briefly summarised.

The use of the microscope as applied to the detection and estimation of different fibres in a sheet of paper has long been known. The first systematic application of quantitative methods to the vegetable fibres and manufactured products is that of Vétillart, embodied in his treatise "Études sur les fibres vegetales textiles." Gottstein, in 1884, we believe, first suggested the quantitative microscopic method of counting the number of mechanical wood fibres in a given field of a specimen carefully mounted using as a test for comparison specially prepared papers containing known percentages of mechanical pulp.

Microscopic Analysis.—The paper is broken up into pulp by preliminary treatment with a weak solution of caustic soda, which is then thoroughly removed by means of hot water, and a number of slides are mounted for inspection, Herzberg's staining reagent being used to colour the mass of fibres. Several slides are so prepared and carefully examined. The examination is best effected by bringing every portion of the slide into the field of view of the microscope, a record being made for each field of view as to the approximate proportion in which the fibres are present. This method is preferable to that frequently employed, of absolutely counting the fibres, but it demands a good deal of previous experience with pulp mixtures in which the proportions are already known.

The usual staining reagents which may be used for differentiating fibres examined under the microscope are various aniline dyes, iodine solutions and iodine combined with dehydrating agents. The most useful reagent for general work is Herzberg's iodine and zinc chloride solution. The formulæ for the preparation of these reagents are as follows:—

Winkler—

Potassium iodide	5 grammes.
Iodine	1 gramme.
Water	20 c.c.
Glycerine	1 ,,

Herzberg—

Chloride of zinc	20 grammes.
Potassium iodide	2·1 „
Iodine	0·1 gramme
Water	5 grammes.

The colorations produced by these reagents are shown in the appended table, but the colour reaction varies with the purity of the fibre, and the percentage of moisture present in the small quantity placed on the microscope glass.

MICRO-CHEMICAL REACTIONS OF FIBRES.

Fibres.	Coloration produced.		
	Iodine solution.	Zinc chloride, iodine solution.	Magnesium chloride, iodine solution.
Cotton, linen, hemp	Brown	Wine-red	Reddish brown
Esparto, straw, bamboo, celluloses	Grey to greyish brown.	Blue to violet, or blue to greyish violet	Bluish violet
Wood celluloses .	Colourless.	Blue to bluish violet	Light brown to red
Manila hemp .	Grey, brown, or yellowish brown.	Dark yellow or greenish yellow	Yellow, greenish yellow
Mechanical wood pulp, jute . .	Yellow.	Yellow	Yellow
Unbleached Manila, straw (partially boiled) .	Yellow.	Yellow.	Yellow

Colour Methods of Analysis.—Various simple colour reactions are known, all of which afford a rough indication of the proportion of mechanical wood pulp in papers. In 1882, Gaedicke proposed the manufacture of a series of standard papers containing varying proportions of mechanical wood, the first paper in the series to consist of pure sulphite, and the last paper of the series containing 95 or 100 per cent. of mechanical wood pulp. On each of the standand papers a solution of aniline sulphate of known strength produced a yellow coloration, the intensity of which was in direct proportion to the amount of mechanical wood pulp. Equal coloration on the standard, and an unknown paper could then be recorded as evidence of equal amounts of mechanical wood pulp, and this reaction would furnish a means for measuring the percentage of ground wood pulp in the paper. The following reagents can be employed for this purpose.

Aniline Sulphate.—4 grammes of the salt dissolved in 100 c.c. of water. This reagent gives a yellow coloration when placed on paper containing mechanical wood pulp.

Phloroglucinol.—2 grammes of phloroglucinol are dissolved in 100 c.c. alcohol and 50 c.c. concentrated hydrochloric acid added. The solution should be kept in the dark. Gives a pink to crimson coloration more or less intense according to the proportion of mechanical wood present.

Ferric Ferricyanide.—Dissolve 1·6 grammes ferric chloride in 100 c.c. of water. Dissolve 3·3 grammes potassium ferricyanide in 100 c.c. of water. Equal quantities of the solutions to be mixed and used only when required. Gives a Prussian blue colour with mechanical wood pulp.

Wurster's Reagent.—2 grammes of dimethyl paraphenylenediamine dissolved in 100 c.c. of water. Gives a deep red colour with mechanical wood pulp and other lignified fibres.

Phenol.—A dilute solution of phenol gives a greenish blue colour with mechanical wood pulp.

Chemical Methods of Analysis.—Rüller in 1887 suggested a method based on the solubility of cellulose in ammoniacal copper oxide. The paper, having been suitably broken up into pulp, is treated with the solution, and the cellulose dissolves fairly quickly, leaving the mechanical wood pulp as an insoluble residue to be filtered, washed, dried, and then weighed. The cellulose estimations obtained by this process are not very satisfactory.

The reaction of the ligno-celluloses with iodine has also been suggested as the basis of a method of quantitative analysis. The paper reduced to the condition of pulp is allowed to remain in contact with a definite quantity of iodine dissolved in potassium iodide. After standing twenty-four hours the amount of iodine left in the solution is determined by titration with sodium thiosulphate, the amount of iodine absorbed being a measure of the amount of mechanical pulp present.

Godeffroy and Coulon proposed a method dependent upon the reaction between lignified wood fibre and chloride of gold. The paper is torn up into fine shreds, divided into two equal portions of convenient weight, and boiled for about ten minutes in a 10 per cent. solution of aqueous ammonia, then thoroughly washed and dried. One portion is burnt for the determination of ash. The second portion is extracted with a hot alcoholic solution of tartaric acid, dried, and then successively extracted with alcohol and ether. The residue left is then boiled for about fifteen minutes with a dilute solution of gold chloride, the latter filtered and removed by washing. The dried fibre containing the adherent reduced gold is then burnt and the weight of ash and gold ascertained. The difference between the ash previously weighed and the weight of ash and gold together, measures the quantity of gold reduced to a metallic state, and the latter is an indication of the proportion of lignified fibre in the sample of paper. Numerous experiments conducted by Godeffroy and Coulon show that under these conditions 100 parts of mechanical wood pulp *per se* will reduce 21·2 parts of gold.

Benedikt proposed a method based upon the reaction between lignified fibre and hydriodic acid, the products of decomposition being added to silver nitrate, with the precipitation of silver iodide. The weight of dry silver iodide is taken as a measure of the mechanical wood pulp present.

The action of chlorine gas on ligno-cellulose is also suggested as the basis of a quantitative method of analysis for mechanical wood pulp. The paper is boiled in a weak solution of carbonate of soda, washed thoroughly with weak acetic acid, and then with hot water until quite neutral. The paper is pressed and exposed in a damp condition to the action of pure washed chlorine gas. After complete chlorination the excess of chlorine gas is blown out of the vessel, and a known volume of water added to the bleached pulp. The quantity of hydrochloric acid in the aqueous solution is determined by titration with standard soda solution.

The acid equivalent to one gramme of various pulps is as follows:—

Mechanical wood pulp .	4·4 c.c.	normal	alkali
Aspen mechanical pulp .	3·5 c.c.	,,	,,
Unbleached sulphite .	0·46 c.c.	,,	,,
Bleached sulphite .	0·03 c.c.	,,	,,

The most recent method devised, by Cross and Bevan is based upon the well-known phloroglucinol reaction. A weighed quantity of the paper previously broken into pulp is placed in a solution of standard phloroglucinol, the strength of which has been previously found. The quantity of phloroglucinol in solution before and after immersion of the fibre is determined by titration with formaldehyde. It has been shown that all lignified fibres possess what may be called a constant "phloroglucinol absorption value."

The details of the process are as follows:—

Two grammes of the material are dried at 100° C. and then weighed. The weighed amount is transferred to a dry flask, covered with 40 c.c. of phloroglucinol solution (made by dissolving 2·5 grammes of pure phloroglucinol in 500 c.c. of hydrochloric acid of 1·06 sp. gr.), shaken and allowed to stand for some hours, preferably all night. The liquid is then filtered through cotton-wool placed in the neck of a funnel. The filtrate is next titrated, 10 c.c. being mixed with 20 c.c. of hydrochloric acid of 1·06 sp. gr. and heated to 70° C. Standard formaldehyde solution (made by dissolving 1 c.c. of 40 per cent. formaldehyde in 500 c.c. of hydrochloric acid of 1·06 sp. gr.) is now added, 1 c.c. at a time, two minutes being allowed to elapse between each addition.

As indicator of the presence of phloroglucinol, a piece of cheap newspaper is used. A red stain is produced in the presence of free phloroglucinol when a drop of the liquid is allowed to fall on the paper.

Towards the end of the titration the stain gradually takes longer and longer to appear on the paper, and finally it is necessary to carefully dry the paper before a Bunsen flame. The end of the filtration is indicated when the stain is no longer perceptible.

10 c.c. of the original phloroglucinol solution are then titrated under exactly the same conditions, the amount absorbed by the ligno-cellulose being obtained by the difference between the two figures. This phloroglucinol absorption value is expressed as a percentage on the dry weight of the ligno-cellulose.

The following values have been obtained: Wood flour, 7·9; mechanical wood, 6·71; jute (best quality), 3·98; jute (average quality), 4·26; sulphite wood pulp, 0·75; and cotton, 0·2 per cent. of phloroglucinol.

For the calculation of the mechanical wood in paper the following formula is used, 8·0 being the absorption value for mechanical wood, and 1·0 that of sulphite pulp, p the absorption value of the dry ash-free sample, and H the percentage of mechanical wood in the paper.

$$\mathrm{H} = \frac{100\,(p - 1{\cdot}0)}{8{\cdot}0 - 1{\cdot}0}$$

Sources of error, and the conditions necessary for the most constant and accurate results are:—

1. The purity of the phloroglucinol used. The standard solution is made from a weighed amount of this substance. It is therefore necessary to ensure its purity.

2. The absorption value is influenced by the concentration of the phloroglucinol solution. The quantities to be used are 2 grammes of paper and 40 c.c. of phloroglucinol solution.

3. Generally, it is unnecessary to remove sizing material from the paper before the determination. In the case, however, of large quantities being present, its extraction

(by warming with a mixture of alcohol and ether) is to be recommended, the reaction taking place more rapidly.

EXAMPLES.

Newspaper.	Ash. Per cent.	Sizing. Per cent.	Phloroglucinol absorption. Per cent.	Mechanical wood. Per cent.
Times . . .	8·4	1·5	2·14	16·3
Daily Telegraph .	2·4	1·5	2·40	20·0
Tribune . . .	10·2	1·5	5·23	60·4
Daily Graphic .	15·1	1·5	5·0	57·1
½*d*. paper (white) .	1·5	1·5	6·62	80·3
½*d*. paper (pink) .	2·0	1·5	6·32	76·0

CHAPTER V

CHEMICAL WOOD PULP

The term "chemical," in contradistinction to the term "mechanical," is applied to wood pulp prepared by a chemical process in which the isolation of the fibre is effected by treatment of the wood with suitable solutions. The resultant product is a more or less pure form of cellulose, differing very materially from the fibre of the mechanical process. In the latter case the pulp consists of the raw wood in which the constituents are unchanged except in form and shape, whereas the chemical pulp is entirely different in composition from the original material. This is shown in an analysis given by Griffin and Little :—

	Spruce wood.	Spruce cellulose.
Moisture .	11·5	6·7
Ash . .	0·3	0·5
Cellulose .	53·0	89·7
Lignin, etc. .	35·2	3·1
	100·0	100·0

The methods employed for the preparation of cellulose from wood are of two kinds, namely, the *acid*, of which the so-called sulphite process is typical, and the *alkaline*, exemplified by the well-known soda process.

Preparation of Wood.—Whichever system is used the preliminary operations for preparing the wood are the same. The logs are cut into lengths of two feet, the bark completely removed by the methods described in the chapter on Mechanical Wood Pulp, and subsequently cut up into small chips by special machinery.

For the best qualities of pulp the knots in the wood are cut out, or as an alternative the chips of wood are carried by means of a travelling band into a sorting room and all the knots and faulty pieces of wood removed by hand.

Sulphite Process.—In general terms this consists in submitting the wood to the action of sulphurous acid and its acid salts in closed vessels at high pressure for definite periods of time. The quality of the product can be varied to almost any extent by the conditions of treatment, that is by varying the strength of liquor, the steam pressure, and the period of time occupied in digestion. This may be shown by a study of the several qualities of sulphite pulp available for paper-making.

Quick Cook Process.—This term is applied to pulp prepared by digesting the wood at a high pressure of 80—100 lbs. per square inch for a period of eight to nine hours. If the operation is carried out to an extreme limit, using the strong liquor, a soft pulp is obtained of good colour which bleaches very rapidly with a small proportion of bleaching powder. If on the other hand the treatment is carried out with a minimum quantity of liquor just sufficient to produce complete disintegration of the wood, then the pulp obtained is of a reddish colour, not easily bleached, but which is characterised by great strength and toughness. The latter kind of pulp is eminently suited for the manufacture of news and wrapping papers, in which strength is of primary importance, whereas the former quality of pulp produced by excessive boiling is more suitable for book papers and writings in which colour is of greater importance.

Slow Cook Process.—This method differs radically from the quick process, in that the pressure is seldom allowed to exceed 15 lbs., while the time of boiling occupies thirty to forty-eight hours. Moreover, the heat is applied by means of steam passed through lead coils so that the condensed steam produced does not accumulate in the digestor itself. The pulp obtained in this case is of excellent quality and of great strength, being particularly adapted for the production of papers such as imitation parchments. It is frequently described as "Mitscherlich" pulp from the name of the inventor of the process.

Sulphite Liquor.—The chemical solvent used in the bi-sulphite process is a solution of bi-sulphite of lime containing a certain proportion of free sulphurous acid. It is prepared by burning sulphur or pyrites rich in sulphur, in suitable ovens, and passing the sulphurous acid gas obtained through tanks containing milk of lime, or through towers containing blocks of limestone moistened with water. Many different systems are in use for burning the sulphur under regulated conditions, and for producing a liquid containing definite proportions of lime or magnesia sulphites and free sulphurous acids. The proportions vary in different mills, the following being typical of many:—

Free sulphurous acid . . .	2·03 per cent.
Combined sulphurous acid . .	1·01 ,,
Lime	0·83 ,,

The quantity of sulphur required per ton of finished pulp varies from 250 lbs. to 400 lbs. Considerable attention is now given to methods by means of which the sulphurous acid gas which comes away from the digestors during the operation is utilised, thereby reducing the amount of sulphur actually required per ton.

Waste Sulphite Liquors.—The waste liquors discharged from the boilers when the wood has been boiled are at present thrown away. Many attempts have been made to recover the by-products, but no system has yet been introduced for the recovery of the sulphur on a large commercial scale likely to be remunerative, or for the manufacture of by-products having any practical value.

The problem has long been a serious one, for in 1894 a prize of 10,000 marks was offered in Germany for a practicable method of preventing the pollution of streams by the waste liquor of sulphite mills, but no serviceable process has been devised. The volume of liquor is so large, that the difficulties are greatly increased. One ton of air-dry pulp gives about 2,500 gallons of acid liquor which diluted with a sufficient quantity of wash waters required for cleaning the pulp blown from the digestors is increased to about 10,000 to 12,000 gallons.

Hoffmann* gives the analyses of several waste liquors as follows:—

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* Hoffmann, C., Practisches Handbuch der Papier Fabrikation, 1897.

ANALYSES OF SULPHITE PULP WASTE LIQUOR.

	Grammes per litre.				
	1	2	3	4	5
Total solids. . .	82·0	88·0	85·0	93·0	92·0
Loss on ignition . .	68·0	75·0	69·0	81·0	—
Ash	14·0	13·0	16·0	12·0	—
Total sulphur . .	—	—	—	—	9·2
Free sulphur dioxide (SO_2)	2·6	2·2	2·9	2·6	3·8
Sulphite radicle (SO_3) .	7·3	7·9	6·7	1·2	3·8
Sulphate radicle (SO_4)	4·1	5·4	4·8	2·7	1·9
Oxygen consumed .	52·0	52·0	50·0	60·0	—

The characteristic constituent of these liquors is[1] the lignone-sulphonic acid (calcium salt) resulting from the specific interaction of the bi-sulphites with the aldehydic or quinonic complex of the wood or ligno-cellulose.

The free lignone-sulphonic acid gives a characteristic reaction with gelatin, precipitating a colloidal viscous mass, which may be re-dissolved in weak alkaline liquids, and when so re-dissolved has been employed in engine-sizing papers. The reaction with gelatin suggests its employment as a "tanning" agent in the manufacture of

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[1] Lindsay and Tollens, Annalen, 267—341; H. Seidel, *Zeitschr. Angew. Chem.*, 1900; Suringar Diss. Gottingen, 1892; *Klason. Chem.* Ztg., 1897, 261; Seidel und Hanak. Mitt. Techn. Gew. Mus. 1897—8.

leathers; and a certain amount of the liquor is being utilised in this industry.

In addition to the characteristic lignone-sulphonic acid, and excess of sulphurous acid, free and combined, the liquors contain a certain proportion of carbohydrates; and hence after treatment of the liquors to bring about the necessary conditions, a process of fermentation is induced by the introduction of yeast, from which alcohol results.

The subject of the composition and utilisation of sulphite liquors has, in fact, been extensively studied, and the following brief account of the processes patented during the last thirty years may be added. Cross and Bevan observed the reaction of the lignone sulphonates and patented the production of the insoluble colloidal compound and its use in the engine-sizing of papers. [E. P. 1548, 1883.]

Mitscherlich revived the method of mixing gelatine or some cheaper form of animal size with the spent lye, in order to obtain a tannin size suitable for sizing paper in the beating engine. By using ordinary rosin size in conjunction with the new product he claimed a reduction in the cost. [D. R. P. 93,944—5.]

Ekman obtained a substance which he called "Dextron" by concentrating the liquors to 34° Bé. and adding magnesium sulphate. The product was applied to the dressing of textile fabrics to render them partially waterproof and to secure them from mildew. [D. R. P. 81,643.]

Dr. Frank proposed the addition of milk of lime to the waste liquor so as to separate the sulphites as calcium sulphite, the remaining liquid to be discharged as comparatively harmless.

The presence of the large proportion of organic matter in the liquor has suggested the basis of a scheme for the manufacture of compressed fuel. Attempts have been made to concentrate the waste liquors to a syrupy consistency and to employ this paste in conjunction with sawdust, coal dust or charcoal for the production of briquettes.

Dorenfeldt patented a modification of the ordinary calcium bi-sulphite process which appeared to make the subsequent treatment of the spent digestor lyes a more profitable undertaking. Sulphate of soda was added to the usual bi-sulphite of lime liquor, whereby a precipitate of sulphate of lime was obtained, and a solution of bi-sulphite of soda. The sulphate of lime was filtered off and sold as "pearl hardening" for the loading of paper, and the bisulphite of soda used for digesting wood. The soda was recovered by concentration and incineration and afterwards converted into caustic soda by the ordinary methods.

Drewson proposed to heat the stronger waste liquors with lime under pressure, the resultant product calcium mono-sulphite being subsequently converted into the soluble bi-sulphite with sulphurous acid gas. The cost of the process and the impurity of the regenerated liquor are conditions which have prevented the development of a likely scheme for recovery. [D. R. P. 67,889.]

Destructive distillation has been experimentally tried, but the yield of useful products is much too low. The formation of oxalic acid by fusion of the concentrated liquor with alkali has also been proved, but the quantity obtained was too small to render any operations on a large scale commercially possible.

"Lignorosin," a substance obtained by converting the lignone-sulphonic acid into a soda salt, has been successfully applied in mordanting woollen goods. Its use in this direction is naturally very limited, and offers no inducement to manufacture on a large scale.

The utilisation of the lignone-sulphonates by treatment with nitric acid for the manufacture of colouring matters is suggested by the reactions of the lignone constituents of wood with nitric oxides. The treatment of these substances with nitric acid gives a series of orange and yellow dyes which produce bright shades on wool and silk. Fusion of "lignone" with sodium sulphide and crude sulphur gives a sulphur dye that colours cotton dark green, changing to black in a chrome bath.[1]

The manufacture of a tanning substitute involves a certain purification of the waste sulphite liquor to eliminate the excess of mineral sulphites, and a certain proportion of soluble iron compounds, which produce discoloration when used in association with ordinary tanning. Considerable activity is being shown in this direction, with some prospect of success.

Robeson has patented a process for tanning skins and hides in which a liquor containing a compound of sesqui-oxide of aluminium or some other base with the practically unchanged organic matter of waste sulphite liquors is employed. The lye is treated with the sesqui-oxide in conjunction with an acid capable of precipitating mineral matter from the liquor.

As 25 per cent. of the solid residue in sulphite liquors

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[1] Pollution of Streams by Sulphite Pulp Waste. E. B. Phelps, U.S.A. Geological Survey Dept.

can be removed from solution by the hide powder test, the process seems promising.

A writer in the *Wochenblatt* has suggested the incorporation of the lyes with soap, claiming that the resinous and glucose substances present together with the mineral salt, would produce a new soap of good lathering and cleansing properties.

Knösel suggests a process for mixing the sulphite lye after suitable concentration with an equal weight of phosphate of lime, thereby obtaining a solid and soluble compound to be used as a fertiliser, the manurial qualities of the phosphate of lime being increased 30 per cent.

Elb adds formaldehyde to the sulphite liquors during concentration and obtains an adhesive substance, clear and transparent, soluble in water. The formaldehyde is said to prevent the separation of salts during evaporation.

Alcohol from Waste Lye.—The most recent and interesting attempt to deal with the waste sulphite liquors is seen in the experiments now being carried out on a large scale in Sweden for the production of alcohol. The process is being worked on a fairly large scale under Ekstrom's patents at Skutskär in Sweden, the average yield of alcohol being 60 litres per ton of cellulose, no less than 54,000 litres having been produced during 1909.

In 1819, Braconnet observed that, by the action of sulphuric acid on wood, grape sugar was formed, which could be fermented to yield alcohol.

In 1898, Simonsen obtained 60 litres of spirit from one ton of wood by this acid process.

In America, Ewen and Tomlinson, acting on the suggestion of Classen, obtained 78 litres of spirit by the action of sulphurous acid on wood.

In 1891, Lindsay and Tollens found 1·2 per cent. of fermentable carbohydrates in the dry solids of waste sulphite liquor, and obtained about 60 litres per ton of cellulose.

Two processes have now been patented in which the lyes are first neutralised by carbonate of lime. In Wallin's method ordinary lime is used for neutralising the liquor, and in Ekstrom's system the waste lime sludge of the sulphate cellulose mills is employed. Schwalbe states that the neutralisation sludge obtained, after the process, contains sufficient calcium sulphite to effect a saving of 40 per cent. of the sulphur required for boiling wood.

The volume of liquor to be treated amounts to 10,000 litres for every 100 tons of cellulose and the dry precipitate obtained on neutralising amounts to 15 tons. The liquid, after being neutralised, is cooled, aerated, then fermented for 72 hours at a temperature of 75° C., by means of yeast, and afterwards distilled. The alcohol obtained contains considerable proportions of methyl alcohol, aldehydes, furfural and acetone. It may be noted that this process, while interesting as showing the possibility of obtaining useful products from the waste liquor, does not deal with the serious problem of the prevention of pollution of streams by the discharge of the waste liquor.

The direct recovery of the original sulphur has not yet been evolved as a satisfactory process. Evaporation and combustion of the concentrated lye means a large loss of sulphur, and a method for the regeneration of the latter from organic sulphur compounds has yet to be discovered. Obviously this is the correct solution of a difficult problem, as it might avoid the formation of a large quantity of by-products which find no useful application in paper-making or any industrial operations.

Washing and Finishing.—The pulp discharged from the digestor is thoroughly washed with water for the removal of the spent liquor, and then subjected to a careful screening in order to remove incompletely digested pieces of wood and any dirt which may be present.

This is effected by screens of various kinds, all based upon the same principle, though differing in construction. The apparatus most frequently employed is the flat screen, consisting of a heavy cast-iron shallow tray fitted with brass plates which contain fine slits. The tray is kept in a state of violent agitation, so that the mixture of pulp and water flowing into the tray is also continuously shaken. By this means the pulp is easily screened, the pure material finding its way through the slits, while the coarse lesser-cooked material remains on the surface of the screen.

The pulp is then sorted up into various qualities, the coarse residue being sold at a low price as " screenings."

The fibre passing through the screens, being mixed with a very large volume of water, is then subjected to a process whereby the water is removed, and the pulp obtained in the form of moist sheets, containing about 50 per cent. of moisture.

Sulphite pulp is usually prepared for export in the form of dry sheets, and these are produced by treating the pulp in a somewhat different manner. The wet mixture is converted into dry sheets by means of a machine which closely resembles an ordinary paper-making machine—that is, the mixture of pulp and water is passed over a horizontal travelling wire and the thin sheet of pulp so obtained drawn through heavy rollers, which squeeze out a large proportion of the excess water, and finally over drying cylinders heated internally by steam.

Soda Process.—The alkaline treatment of wood for the manufacture of soda wood pulp is similar to that used for the manufacture of esparto pulp. The wood, in the form of small chips, is heated in large digestors with a solution of caustic soda. The non-fibrous constituents of the wood are completely dissolved, and a brown-coloured pulp is obtained. The spent liquors are preserved and the soda recovered, to be used over again as required.

The soda process is one capable of general application, being utilised for woods and fibres which cannot easily be treated by the sulphite process, which latter is usually confined to the treatment of the coniferous woods. In the early days of the manufacture of wood pulp, when spruce was available in large quantities, wood pulp was almost exclusively prepared from spruce by the sulphite process. The present scarcity of spruce and the high price now ruling have compelled manufacturers to give their attention to other classes of wood, and the American Government, for example, are making investigations as to the use of woods which have hitherto been regarded as unsuitable. Such investigations will, no doubt, lead not only to the introduction of woods other than spruce, pine, and poplar, but also to modifications in the various methods of treatment.

All kinds of wood and other fibrous material may be converted into pulp by this process. Caustic soda combines with the acid products derived from the non-fibrous constituents of the wood until the alkali is neutralised, so that the insoluble portion of the wood left is cellulose in a more or less pure condition, containing much less resin than the pulp obtained by the sulphite process.

The practical operations are simple enough. The wood is barked in the usual manner and cut up into small pieces by the same machinery as that employed for the sulphite process. The wood is digested for six to eight hours in a solution of caustic soda having a strength of about 20° Tw., at a pressure of 100—150 lbs. per square inch. The conditions of treatment are varied according to the nature of the wood and the requirements of the paper manufacturer. For pulp that will bleach readily the process of digestion is carried out to a greater extent than for pulp which is required in the manufacture of wrapping papers. The yield of pulp and the quality are influenced by these conditions.

Some interesting experiments were made by Beveridge showing the precise influence of varying factors. He made three sets of trials as follows :—

	Constant condition.	Variable.
1.	Time and strength of caustic	Pressure varied.
2.	Pressure and time	Strength of caustic varied.
3.	Pressure and strength of caustic	Time varied.

The results were :—

(1) The increase of pressure resulted in a diminution of yield, the quantity of pulp obtained being reduced considerably.

(2) The excess of caustic soda caused rapid diminution in the yield of cellulose.

(3) The gradual exhaustion of the caustic soda by a prolonged digestion prevented such serious diminution of yield.

From a practical standpoint the chief consideration is the nature of the wood, and De Cew gives the following results as showing the usual conditions of treatment:—

Wood.	Weight of one cord 128 cub. ft. Lbs.	Caustic soda used per cord.	Weight of air-dry pulp from one cord. Lbs.	Yield air-dry pulp. Per cent.
1. Yellow Birch .	3630	641	1610	44·4
2. Soft Maple .	3520	641	1560	44·4
3. White Birch .	3190	603	1490	46·7
4. Poplar . .	2350	603	1150	49·0
5. Bass wood . .	2325	603	1135	49·0
6. Black Spruce .	2250	678	1000	44·5
7. Hemlock . .	2300	716	970	42·2

The variation in the quality of the pulp produced by the soda process is a striking illustration of the necessity for an exhaustive study of the whole process of chemical wood pulp manufacture. The most interesting developments are seen in the suggestion that the highest yield of pulp consistent with the complete removal of the non-cellulose portion of the wood is best obtained by modifications in the process, which reduce the action of the caustic soda on the cellulose to a minimum. Suggestions have been made in this direction not only with the soda process, but with all chemical methods by the idea of using wood in a perfectly dry condition; by having a vacuum inside the digestor, so that the air is largely removed from the pores of the wood, enabling the liquor to penetrate quickly; by the use of superheated steam for the boiling operation; and so on.

All these improvements are in the right direction, because the wood is not subjected to a more severe treatment, but is merely placed under more favourable conditions for the action of the caustic soda. The result of these various improvements is seen in the fact that many hard woods can be reduced to the conditions of an easy bleaching pulp in three and a half to four hours. Another instance of the value of modified conditions is to be seen in kraft papers.

Kraft Paper.—The term "kraft," meaning strength, has been applied to certain strong wrapping papers made by submitting wood to a modified soda process. The paper is remarkably tough, possesses a high tensile strength, and is a striking testimony to the possibilities of wood pulp as a material for making a great variety of papers. It is said that the process was discovered accidentally by a pulp manufacturer who, rather than waste some soda pulp which had not been sufficiently digested, placed the half-boiled wood in an Edge runner or Kollergang, and reduced it to pulp by the simple process of friction. The paper finally obtained proved to be so firm and strong that the success of the new "discovery" was assured.

The process, as usually carried out, involves the digestion of the wood in a soda or sulphate liquor containing about 30 per cent. of the black lye from some previous cook. The wood is not completely boiled, but digested to a point at which the fibres can be disintegrated by simple friction. The undissolved ligno-cellulose acts as a useful cementing material, and the paper is bulky, light and strong.

The success of the so-called "kraft" papers made from soda pulp has led to the production of imitations, manufactured chiefly from sulphite pulps. The true kraft papers may be distinguished from the imitations by various differences in appearance and behaviour. The sulphite papers have a smooth, shiny surface when viewed in reflected light and held up on a level with the eyes, but this is only appreciated by a practised observer. The soda papers are tougher and capable of resisting a greater amount of friction, as may be proved by the well-known crumpling test. They can be twisted repeatedly without producing fracture, and this is a desirable feature in papers used for the manufacture of bags. The behaviour on tearing is generally different in the two papers, the soda being more resistant.

The sulphite papers have a lower tensile strain, as a rule, than soda papers of equal weight, and also a lower percentage stretch or elongation under tension.

These differences in physical qualities may be used as a means of discriminating between real and imitation kraft papers.

It may further be noted that the natural self-colour of soda kraft papers is artificially imitated in the sulphite krafts by the use of yellow aniline dyes, which can be readily extracted by means of hot water, weak solutions of alkali, or rectified alcohol. The paper after treatment is quite another colour, and this in itself is evidence of a useful character.

If small pieces of the paper are pulped and boiled in a solution of malachite green, the soda paper is dyed to a much darker colour than the sulphite.

When the pulp is examined under the microscope, the pitted cells in the fibres of the soda pulp contain a little nucleus of green colour, which is easily detected. This test is not of much value, since many of the fibres even of the soda pulp do not show any strongly marked pitted vessels.

Soda Recovery.—In the treatment of wood and other fibres by the soda process, at least 50 per cent. of the weight of raw material is dissolved, the yield of paper pulp being about 45—50 per cent. The soluble soda compounds formed during the operation are rich in organic matter, and advantage is taken of this fact to recover the soda used. The black liquors discharged from the digestor are stored in tanks, together with much of the water used for washing the boiled pulp, and then concentrated by some system of evaporation. When the liquors are sufficiently concentrated, a thick pasty mass is obtained containing a large proportion of organic resinous matter, and this on being submitted to the action of a furnace catches fire and burns. The substance is thereby converted into a dry burning mass, and after the combustion is completed the resultant material consists mainly of impure carbonate of soda.

The whole process is one that calls for considerable skill and attention, particularly in the methods employed for utilising all the available heat. The cost of evaporation of the liquors and subsequent combustion of the black liquor is reduced to a minimum by a carefully regulated system of washing in order to prevent the accumulation of a large volume of weak washing waters, and by the utilisation of the waste heat obtained by the combustion of the organic soda compounds in the concentrated liquor.

The following description of a modern recovery plant will afford some idea of the process.

When the digestion of the wood or fibre is complete, the hot black lye is discharged from the digestors into storage tanks, which are usually fixed above the combustion chambers so as to maintain the temperature and prevent loss of heat. The fibrous material in the digestor is then washed with hot weak washings from some previous boiling, and lastly with hot clean water. The final washings only contain a small percentage of soda, and these are utilised as far as possible for a preliminary treatment of fibre from which the strong black lye has just been removed. The systems of washing vary in different mills, but the main object is the same in all cases, viz., a maximum recovery of the soluble soda compounds with a minimum volume of water.

The evaporation of the black lye is effected by the use of a Porion furnace or a multiple-effect evaporator.

The *Porion Evaporator* consists of a number of shallow pans built of brick, arranged in the form of an enclosed chamber, on the top of which are placed the tanks containing the liquor to be treated. A furnace at one end supplies heat, which sets fire to the concentrated liquor in the adjacent pan, and the heat derived from the combustion of the thick lye is utilised in further evaporation of the liquor in the other pans and chambers. The Porion is in effect an evaporator and incinerator.

The *Multiple-effect Evaporator* is based upon the systematic utilisation of heat and reduction of pressure in the containing vessels, in series, so as to produce maximum vaporisation effect per thermal unit. The spent liquors are pumped through a series of tubes contained in several cylindrical vessels, the tubes of the first vessel being treated externally by steam at a pressure of 15—20 lbs. The liquor passing through the tube is raised to boiling point, and on being discharged into a separating chamber gives up the steam produced. The steam so liberated then becomes the heating agent for the series of tubes in the second cylindrical vessel, and the partly concentrated liquid falling to the bottom of the separating chamber is drawn by a vacuum through the tubes of the second vessel, which are therefore under reduced pressure. The process is repeated through three or four systems of tubes, in each case the steam liberated in the separating chamber being used to produce a further concentration of the liquor.

An apparatus of this kind will reduce 2,000 gallons of liquor per hour, having a specific gravity of 1·050 to 400 gallons with specific gravity 1·250, evaporating off 1,600 gallons of water per hour.

The concentrated liquor leaving the evaporator is discharged into storage tanks and then allowed to flow continuously into a rotary furnace. The thick lye catches fire, burns with a steady flame, and is discharged as a black mass still burning, which is wheeled away, and allowed to char until the black carbonaceous matter has completely burnt off.

Sulphate process.—First introduced by Dahl in 1883, for the treatment of straw, but now considerably applied to coniferous woods which do not soften under the soda treatment as the foliage of dicotyledenous woods.

Sulphate of soda from which the process derives its name is of course inert, *i.e.* without action upon the wood substance and is added as a source of alkali, and to make good the mechanical losses in the process of recovery of the soda.

This loss is approximately 10 per cent. From an analysis of sulphate liquor (see later) it is seen that there is a large proportion of sodium sulphide ; this is not added as such, but is formed by the reduction of the sulphate to sulphide in the process of recovery when the residue is ignited, this reduction being effected by the soluble organic matter in combination with soda.

The sulphide has a hydrolysing action, similar in character to caustic soda, but has another function in that it has the effect of aiding the splitting of the lignone complex from the cellulose proper. This dissociating characteristic is clearly seen when wood is treated with a mixture of sodium sulphide and hydrate, as against caustic alone of the same soda content.

The general manufacture of sulphate pulp is restricted, for though the process yields an excellent pulp, yet the evil smelling compounds formed by the interaction of the sodium sulphide with the organic matter, limits its production to sparsely populated districts, as in Germany and Austria.

ANALYSIS OF SULPHATE LIQUOR.

Sodium sulphate	37 per cent.
Caustic soda	24 per cent.
Sodium sulphide	28 per cent.
Sodium carbonate	8 to 10 per cent.
Sodium acetate	2 to 3 per cent.

Soda and Sulphite Pulps.—Although at one time the woods employed for the production of sulphite pulps were almost exclusively pine and spruce, and the soda process was applied chiefly to poplar and dicotyledonous woods, the two processes are now used almost indiscriminately for any wood capable of yielding a paper-making fibre.

It is exceedingly difficult to differentiate the processes by an examination of the chemical or microscopical characteristics of the fibres or the pulp, especially when the pulps have been bleached. There are certain broad distinctions between pure unbleached soda and unbleached sulphite pulps which can be readily noted, but these are not easily detected in papers containing a mixture of the two.

It is impossible to state with any certainty that a bleached soda paper does not contain sulphite pulp, though any marked deviation from qualities expected in a soda paper would indicate the presence of sulphite pulp. If the soda pulp has been made from poplar wood, it is easily detected, and the admixture of any spruce may be approximately determined, but if the soda pulp has been made from spruce, no satisfactory analysis is possible.

The differences between soda and sulphite pulps, even when prepared from the same type of wood, may be found in the physical qualities, since the soda pulp is of a light brown colour, soft and bulky, and very tenacious, while the sulphite pulp is reddish white, harsh, strong and less bulky. The presence of a much larger percentage of natural wood resin in sulphite pulp, namely, 0·5 per cent., as against 0·05 per cent. in soda pulp, can be used as the basis of a test, but it is of no value for sized papers.

A small quantity of the pulp is heated continuously with carbon tetrachloride. The solution placed in a fresh test tube is mixed with an equal volume of acetic anhydride, cooled, and added to a few drops of concentrated sulphuric acid. With soda pulp no definite reaction occurs, but with sulphite pulp a pink coloration changing quickly to green is produced.

THE BLEACHING OF WOOD PULP.

Two methods are in use for the bleaching of wood pulp, the most general being the employment of ordinary bleaching powder, and the second being the treatment of the pulp by means of solutions of hypochlorite of soda or magnesia prepared by electrolysing the chlorides. This method of electrolytic bleaching is finding general favour amongst manufacturers when the power required can be supplied at a cheap rate.

Bleaching with Chloride of Lime.—The general principle of bleaching wood pulp by means of a clear solution of ordinary chloride of lime is simple and fundamentally a process of oxidation. The method consists in immersion of the pulp in a given quantity of diluted bleach liquor of definite strength, but many modifications of method are available, and need to be closely studied in order to produce the best results economically. The various systems in use may be briefly described.

Bleaching in the Potcher. — This is the process most generally adopted by the paper-makers. The sheets of dry pulp are put into the potcher with water, broken up, and a definite volume of clear bleach liquor is added. The pulp is continuously circulated until the desired colour has been obtained, or until the bleach has been completely exhausted.

When the operation is completed, the pulp is washed continuously with fresh water, the exhausted bleach liquor and washings being removed in the usual way by means of the drum washer. In many cases the pulp is discharged into large tanks provided with perforated false bottoms and the washing process completed by draining.

Bleaching in Drainers. — A modification of the above process which gives good results is frequently used. The pulp is broken up in the potcher, the requisite amount of bleach liquor is added and the contents of the potcher at once discharged into tanks where the bleaching process is allowed to proceed with the mass at rest. This method requires longer time, but gives excellent results in point of colour and economy of bleach.

Bleaching by the Tower system.—For this process of continuous bleaching a series of cylindrical vessels with tapering bases is used, about 16 to 20 feet high and 8½ feet in diameter.

The stuff is kept in circulation by means of a pump fitted at the junction of the tapering ends with an external pipe, the latter being so arranged that the circulating stuff can be pumped into the tower or to the adjacent one of the battery.

Fitted in the upper part of the tower is a cone, arranged centrally with, and almost touching, the sides of the outer cylinder to ensure thorough distribution of the stuff, as it is pumped up the external pipe (see Fig. 19).

It is usual in a modern battery of bleaching towers to pass the stuff as it comes up from the potcher through a concentrator in order to remove a large proportion of water whereby the bleaching is carried out more economically and expeditiously.

In series with the last bleaching tower also there is a second concentrator, which removes the residual bleach liquor to a great extent, the necessary washing being reduced thereby to a minimum.

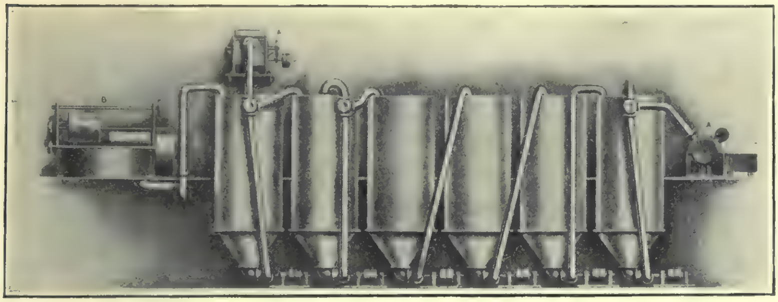


Fig. 19.—Tower Bleaching Plant.

This photograph on a reduced scale represents a plant capable of bleaching 10 tons of half stuff per diem.

This machine is very simple and compact, and capable of a large output.

It is on this account to a certain extent replacing the more costly presse-pâte system of purification. It consists of a revolving drum made with a central internal cone, so as to deliver water at both ends. The shell itself is of brass, drilled with holes and covered with a wire cloth. The stuff is pumped up through a butterfly throttle valve into a splaying mouth, thus causing the pulp to flow along the whole width of the drum cover.

The cover or hood is so arranged by means of packing, that the water in the half-stuff can be forced through the wire cloth of the revolving drum, by a pressure of 2 to 3 lbs. per square inch, leaving a mat of fibre upon it.

The pulp is then picked off the wire by means of a jacketed couch roll, and a wooden doctor fitted to the latter serves to scrape off the fibre into boxes. An economy of about 25 per cent. in the bleach consumption over the ordinary method employed with a minimum of power is claimed by this system. The total time occupied in bleaching is usually about twelve hours without heat.

Automatic Process. — In many wood pulp mills the "tower" system is so contrived as to produce a continuous automatic bleaching of the pulp. The pulp discharged from the digestors is thoroughly washed and then pumped into a series of large cylindrical vessels, so arranged that a continuous stream of pulp and water enters the first vessel together with a carefully regulated quantity of bleach liquor which also flows into the first tank at a constant rate. The mixture gravitates into the second vessel of the series, then into the third, and in this way through all the vessels, until on reaching the last tank the bleach is fully exhausted and the pulp has attained the desired colour. The bleached pulp is then removed and thoroughly washed.

Conditions for Economical Bleaching.—It is difficult to accurately compare the methods adopted by paper-makers in bleaching wood pulp for the purpose of determining which system gives the best results, but there are certain conditions common to all methods.

In the first place, the bleaching powder must be of good quality, containing the specified percentage of available chlorine. The extraction of the soluble calcium hypochlorite also needs careful attention, as serious losses frequently occur when the powder is not properly exhausted.

With chloride of lime containing 35 to 36 per cent. of available chlorine the quantity of clear bleach liquor obtainable for various densities is shown in table:—

TABLE SHOWING THE NUMBER OF GALLONS OF BLEACH LIQUOR OBTAINED FROM 1 CWT. OF POWDER (34 TO 36 PER CENT. OF CHLORINE).

Twaddell.	Available chlorine. Lbs. per 100 gallons.	Gallons from 1 cwt. 34 per cent. powder.	Gallons from 1 cwt. 36 per cent. powder.
20	61·50	61·2	66·0
19	58·40	65·3	69·0
18	55·18	69·0	73·0
17	52·27	73·5	77·0
16	48·96	77·7	82·5
15	45·70	84·0	88·25
14	42·31	90·0	97·5
13	39·11	98·3	104·2
12	35·81	106·4	112·5
11	32·68	116·5	120·5
10	29·61	129·0	137·2
9	26·62	142·0	151·5
8	23·75	160·3	169·7
7	20·44	186·1	197·2
6	17·36	219·5	232·4
5	14·47	264·0	278·6
4	11·44	334·0	352·5
3	8·48	448·2	475·5
2	5·58	681·0	722·6
1	2·71	1403·0	1488·0
½	1·40	2725·0	2883·0

Any deviation from the above figures may be traced to an unnecessarily prolonged agitation of the powder with water or an imperfect washing of dregs. Fifteen minutes is sufficient to produce a liquor of maximum density with a residue which settles readily; if the operation is continued, as it often is, for an hour or more, the insoluble residue becomes bulky and does not settle quickly. The result is that the first strong liquor cannot be so completely siphoned off from the residue. The best plan is to exhaust for fifteen minutes, allow the sediment to settle completely, siphon off as much as possible, and to agitate the residue for another fifteen minutes with fresh water, adding the weak liquor when clear to the first extract, so as to give a stock bleach liquor for use in the mill at a density of 6° Tw. The dregs are again exhausted with water and the weak liquor so obtained utilised in exhausting the next batch of powder.

It should also be noted that fresh liquors cannot be kept indefinitely in store tanks without deterioration.

The unstable nature of solutions of bleaching powder, and the loss of available chlorine entailed when the liquor is not used under proper conditions, is well known to most paper-makers, although such depreciations in bleaching value are not always expressed in numerical terms. The following experiment will throw some light on the character and extent of the changes found in ordinary bleach liquor, when stored.

Some fresh bleaching powder was taken, and a solution made by extraction with distilled water, having a strength of 7° Tw. Three samples of liquor were put aside under the following conditions:—

A. Sample of clear liquor in stoppered bottle.

B. Sample of liquor in an open vessel, and left exposed, the crust of chalk which quickly formed on the surface being left undisturbed.

C. Sample of liquor in an open vessel, agitated twice a day, at 9 a.m. and 4 p.m.

These solutions were tested once a week, with a standard decinormal solution of arsenic.

TABLE SHOWING C.C. OF ARSENIC SOLUTION REQUIRED BY 1 C.C. OF THE BLEACH LIQUOR.

Period.	A. Stoppered bottle.	B. Open vessel, not disturbed.	C. Open vessel, agitated.
At start	7·05	7·05	7·05
After 1st week . .	6·90	6·90	3·90
,, 2nd ,, . .	6·85	6·60	0·40
,, 3rd ,, . .	6·8	4·0	0·27
,, 4th ,, . .	6·8	2·7	0·15

In the case of the bleach liquor preserved in a bottle and kept away from contact with air, the loss of available chlorine is very slight. In the open vessel, where the formation of a crust has prevented continual contact with air, the reduction of strength is slight the first two weeks. Probably the rapid fall in the later weeks of the period may be due, in some measure, to the disturbance of the crust in removing samples for titration. In the case of the solution agitated each day the loss of strength is very rapid.

The precise value of these changes are readily seen by reference to the accompanying tables, in which the losses are set out.

TABLE SHOWING AVAILABLE CHLORINE IN 100 C.C. OF THE BLEACH LIQUOR.

	A. Grammes.	B. Grammes.	C. Grammes.
At start	2·50	2·50	2·50
After 1 week . . .	2·45	2·45	1·38
,, 2 weeks . . .	2·43	2·34	0·14
,, 4 ,, . . .	2·40	0·96	0·05

Expressing these results in a form more familiar to paper-makers—that is, in terms of the weight of normal bleaching powder—we get the following:—

TABLE SHOWING THE AVAILABLE CHLORINE EXPRESSED AS LBS. OF NORMAL BLEACHING POWDER PER 100 GALLONS.

	A. Lbs.	B. Lbs.	C. Lbs.
At start	70·5	70·5	70·5
After 1 week	69·0	69·0	39·0
,, 2 weeks . .	68·5	66·0	4·0
,, 4 ,, . .	68·0	27·0	1·5

The storage of the bleach liquor in the paper mill usually resembles the conditions of experiment B, and it will be noticed that the depreciation for the first week is very slight indeed.

The principal chemical change brought about by exposure to air is the disappearance of calcium hypochlorite and the increase in the percentage of calcium chloride, concurrent with the formation of a considerable amount of chalk, more particularly with the sample agitated each day.

Use of Residual Liquors.—The practice sometimes adopted of utilising residual liquors washed out of the potcher on the completion of a bleaching operation cannot be generally recommended.

"Back liquors" may be reported as containing "available chlorine" in useful quantity from the density as tested by the hydrometer, in conjunction with the occasional application of the usual chlorine test solution, viz., starch paste and potassium iodide. The latter test, however, has no quantitative value, and the usefulness of the hydrometer as an indirect indicator of *chemical* strength depends upon the correct interpretation of *density*. Direct chemical tests are alone able to reveal the actual condition of the back liquors.

Circumstances under which residual liquors could be used with any advantage are to be found in mills where water is scarce. In such cases the pulp from boiling operations might be treated with the residues for the purpose of using up any traces of bleach, and also economising washing waters.

Composition of Residual Liquors.—The liquors left after the bleaching of wood pulp are of a complex composition, They contain soluble organic compounds, resinous matters. lime salts, residual hypochlorites and salts of higher oxides of chlorine (acids), *e.g.*, chlorites and chlorates.

Temperley gives the analysis of such a wood pulp liquor as follows:—

	Lbs. per 1,000 gallons.
Mineral residues, chiefly calcium chloride	126·6
Organic residues, volatile on ignition .	62·0
Total solids, dried at 100° C. .	188·6

The surface scum obtained from the liquor had the following composition:—

	Lbs. per 1,000 gallons.
Resinous matter	2·17
Lime.	·80
Moisture	8·90
Fibre	2·40
Total . .	14·27

The compounds in solution in residual liquors are very unstable, and react easily with the hypochlorite of fresh bleaching powder, so that the employment of washings in conjunction with raw bleach solution must result in a waste consumption of powder per ton of air-dry pulp.

Temperley has shown this by some interesting experiments, and we quote these as illustrating an important factor in economical bleaching. Definite quantities of bleach solution were added to known volumes of ordinary water, and similarly to equal volumes of a carefully filtered residual liquor from the bleaching of a sulphite pulp. The solutions were tested for a period of four hours at different temperatures, the results being very different in character.

EXPERIMENTS WITH ORDINARY WATER.

Solution.	Temperature used.	Bleaching powder used. Grains per gallon.	Bleaching powder used. Lbs. per 1,000 gallons.
Water	70° Fahr.	4·20	0·60
,,	90° ,,	4·90	0·70
,,	120° ,,	9·10	1·30

EXPERIMENTS WITH RESIDUAL LIQUORS.

Solution.	Temperature used.	Bleaching powder used. Grains per gallon.	Bleaching powder used. Lbs. per 1,000 gallons.
Liquor	70° Fahr.	194·20	27·70
,,	90° ,,	248·50	35·50
,,	120° ,,	784·00	112·00

The figures here show that residual liquors, even if colourless, are positively detrimental to efficient bleaching. Practical work demonstrates this, not only from the point of view of consumption, but, what is often of greater importance, from the point of view of colour. The same defect is found to a lesser degree in the use of unfiltered water, or water coloured by vegetable matter in solution.

It is evident, therefore, that the practice of using residual liquors should be confined to their use for partial washing, and that they should not be used for diluting strong bleach liquors.

There are many interesting and important details to be noted in connection with the bleaching of wood pulp. The process is frequently hastened by the use of live steam, which is blown into a mixture of pulp in the potcher. The rate of bleaching is thus considerably hastened, but the practice is not one that should be carried to an extreme. The economy of bleach is also controlled to some extent by the proportion of water to pulp. In some cases the number of pounds of air-dry pulp per gallon of liquid is much lower than it need be, and this usually tends to a greater consumption of bleach powder. The usual proportions are:—

Air-dry wood pulp . . .	100 lbs.
Amount of solution in potcher	160 gallons.

The bleaching of very hard sulphite pulps not manufactured originally for bleaching may frequently be assisted by slight modifications in the process. A refractory pulp may often be bleached to a good colour by the operation known as "successive bleaching." The pulp is treated with a certain proportion of bleach liquor, which is then washed out and followed by a further quantity of fresh bleach liquor. This method is often sufficient to remove the yellow tinge found in half-stuff from poor qualities of pulp.

Caustic soda may sometimes be used with advantage as a preliminary process in bleaching hard pulps which exhibit a reddish colour, but it is not economical to bleach "low boiled" pulps, as the bleach consumption is too great, sometimes reading 30 per cent. Even simple washing with hot water before bleaching gives a pulp of greatly improved colour.

The improvements due to preliminary washing may be traced to the presence of soluble constituents, the nature of which is at present unknown. That these constituents exercise a considerable influence on the bleaching may be seen from the following experiment:—

PULP BLEACHED FOR THREE HOURS AT 70° FAHR.

Conditions of bleaching.	Per cent. bleach consumed.	Colour.
Pulp bleached in the ordinary way in a shallow dish	10·8	Moderate.
Pulp bleached in the ordinary way in a bottle	10·8	,,
Pulp bleached after being first extracted with water . . .	12·0	Good.
Pulp bleached after extraction with water followed by ether . .	7·6	Very good.

The "time element" is an important factor in many mills owing to the lack of adequate bleaching plant, which in many cases can be attributed to the fact that the output of paper is increased by additional machines, but that this is not accompanied by the installation of further plant for the preliminary operations. Some pulps bleach quickly and readily, while others occupy a much longer time. It is not, of course, possible to determine whether a pulp will bleach easily by mere superficial observation; this can only deal with the associated characteristics of the pulps. The rate of bleach consumption is a close index of general bleaching quality, and the following experiment is of interest as showing the differences between pulps which do not exhibit any great differences when simply judged on external characteristics:—

Experiment 1.—Brand C. An ordinary soda wood pulp. 50 grammes air-dry pulp with 450 c.c. bleach liquor at 65° Fahr. (containing bleach solution equivalent to 11·7 grammes of dry bleaching powder).

Experiment 2.—Brand B. A sulphite pulp. About 14 per cent. of bleaching powder, calculated on the air-dry weight of pulp, added. Actual consumption for colour required amounted to 12·5 per cent.

Experiment 3.—Brand A. A sulphite wood of good colour, requiring a consumption of 8 per cent. of bleach.

Setting out in tabular form the rate at which the amount of dry bleaching powder is consumed, the following results are obtained, expressed in terms of the percentage rate. The total bleach added is taken as 100, and the proportions consumed each hour are taken as percentages of the total:—

RATE OF CONSUMPTION.

Hours.	Brand C.	Brand B.	Brand A.
0	·0	·0	·0
1	33·0	—	20·0
2	44·0	30·0	33·0
3	51·0	—	43·0
4	66·0	55·0	49·0
5	70·0	—	56·0
6	—	78·0	63·0
7	80·0	90·0	70·0

It will be noticed that in none of these cases was the total bleach consumed in the seven hours. If the figures are plotted out on a curve, the differences in behaviour become very clear and may be expressed in definite form.

Thus, with Brand C the pulp bleaches very rapidly during the first hour, and then bleaches at a uniform rate for the succeeding four hours, and subsequently consumes bleach very slowly.

In the case of Brand B, the pulp bleaches somewhat rapidly during the first hour, and then the rate of consumption is quite uniform for the following six hours.

Finally, with Brand A the pulp, in common with most brands, consumes bleach rapidly at first, but afterwards the rate of consumption gets slower and slower.

These three brands are typical of the conditions which will occur with the majority of pulps. The rate of consumption beyond the period of seven hours is not of immediate interest to the paper-maker, but it is still a question of some moment in an investigation of this kind.

Owing to the great differences between pulps as to their bleaching qualities, it is important to have methods for determining the amount of bleach consumed in bringing the pulp to any desired colour. The following methods may be adopted :—

The Approximate Method of Determining the Consumption of Bleach.—The behaviour of the pulp when brought into contact with bleach solution can be studied by paper-makers to some extent without special appliances or chemicals, provided they possess some fairly sensitive balance and a few measuring vessels. The following rough-and-ready method may be adopted with advantage in many circumstances, although the results are only approximate, and cannot be accepted as correct enough for purposes of settling any disputes :—

Take 200 grammes of the pulp and wet out in warm water; place in a large bottle with a further quantity of water; add a few beads or, better, garnets, and shake vigorously. Most pulps can be broken up sufficiently for the laboratory test in this way. Strain off in a sieve, squeeze out excess of water, and divide the moist mass into a number of equal parts, *e.g.*, 10 portions, so that each lot represents 20 grammes of the original air-dry pulp. Pulps which will not break up easily by this method are reduced with pestle and mortar to the required condition of complete disintegration. Unless the pulp is thoroughly broken up, the mass bleaches unevenly and does not give uniform results.

Now to each portion, in a convenient open vessel, add 200 c.c. water and varying quantities of clear bleach liquor from mill stock, so as to obtain a series of bleaching tests. If the mill stock of liquor stands 6° Tw., then it is sufficient to take the following data :—

1 gallon of 6° liquor = ½ lb. of good bleaching powder.

1,000 c.c. of 6° liquor = 50 grammes of good bleaching powder ; 1 c.c. = ·050 grm.

From this assumption it is possible to work out the several quantities of liquor required in the experiment suggested.

The following table shows the necessary volumes of liquor for certain percentages of dry powder :—

No.	Grammes of air-dry pulp in mixture.	Percentage of dry bleaching powder to be added.	Actual weight of dry powder required.	Volume of bleach liquor to give the weight of powder stated.
1	20·0	2·0	0·4 grms.	8·0 c.c.
2	20·0	4·0	0·8 ,,	16·0 ,,
3	20·0	6·0	1·20 ,,	24·0 ,,
4	20·0	8·0	1·60 ,,	32·0 ,,
5	20·0	10·0	2·00 ,,	40·0 ,,
6	20·0	12·0	2·40 ,,	48·0 ,,
7	20·0	14·0	2·80 ,,	56·0 ,,
8	20·0	16·0	3·20 ,,	64·0 ,,
9	20·0	18·0	3·60 ,,	72·0 ,,
10	20·0	20·0	4·00 ,,	80·0 ,,

If all these mixtures are started simultaneously, it is only necessary to stir them occasionally and to note the time at which the bleach liquor in each becomes exhausted. The time of exhaustion is determined by means of starch and iodide test papers, which give a blue coloration as long as the mixture contains any available chlorine. The observer will then add another column to the above table, setting out the various periods of exhaustion.

This experiment not only serves to bring out clearly the rate of consumption, but also gives information as to the amount of bleach required to produce a certain result in reference to colour. For example, the colour gradually improves from test No. 1 up the scale towards No. 10.

In the case of a pulp which requires about 16 per cent. of dry bleach, the changes in colour between tests numbered 7 and 8 will be very slight. Test No. 8 may represent a maximum of colour with a certain percentage of bleach, which maximum it may not be necessary to reach for the particular paper being manufactured. This is a matter for the paper-maker to decide.

Standard Method.—A more accurate method of determining the amount of bleach required for pulp, and one which might be acceptable as a standard official method, is given in the form of instructions as follows:—

Selection of Samples from Bulk.—From the bales of pulp delivered into the mill select 2 per cent. of the number of bales. From each of the selected bales remove one sheet. The sheets so obtained should then be divided into two portions, one of which is to be retained for purposes of reference and the other portion utilised for the laboratory test.

Selection of Laboratory Test Samples.—Cut small strips ¼ inch wide, and any convenient length of 2 or 3 inches from each of the sheets in the bulk samples, sufficient to give three or four lots of about 10 grammes each.

Preparation of Bleach Liquor.—Make up a bleach solution containing 40 grammes of good powder per 1,000 c.c. This gives a 4 per cent. (vol.) solution, which is a convenient working strength. If 40 grammes of good bleaching powder are thoroughly mixed with water and filtered, the residue being properly washed and the filtrate made up to 1,000 c.c., the final solution is of such a strength that 4 c.c. of standard arsenic solution is equal to 1 c.c. of the clear bleach liquor. This figure will vary according to the quality of the powder and the completeness of the washing of the powder. The solution should be carefully standardised with decinormal solution of arsenic, so that the percentage of available chlorine is known, and the exact number of c.c. giving 1 gramme of 35·5 per cent. bleaching powder, calculated. The convenience of making up the solution in this way is obvious. If we assume a good bleaching powder as one containing 35·5 per cent. available chlorine, then

$$1 \text{ c.c. standard arsenic} = \begin{cases} \cdot 00355 \text{ grm. Cl. or} \\ \cdot 01 \text{ grm. bleaching} \\ \qquad \text{powder.} \end{cases}$$

$$25 \text{ c.c. bleach solution} = 1 \cdot 0 \text{ grm. bleaching powder.}$$

Preparation of Test Sample.—Weigh out exactly 10 grammes of the pulp from the selected test sample, macerate and beat in a mortar with successive small quantities of water, using for this purpose 50 c.c. Place the mixture in a beaker, standing this in a water bath, by means of which the mixture can be heated.

The object of using a measured quantity of water, 50—60 c.c., is to ensure that the final mixture of pulp and bleach contains a definite proportion of solution to the amount of dry pulp taken for the experiment, reasons for which have already been discussed.

Bleaching.—Add 62·5 c.c. of bleach liquor to the contents of the tumbler, stir with a glass rod, and add 47—50 c.c. of water.

The proportion of solution to air-dry pulp varies considerably in different mills. The average of figures which have been placed at the disposal of the writer would indicate that the following proportions might be utilised for purposes of experiment:—10 grammes of air-dry pulp and 160 c.c. of solution. With regard to the amount of bleach liquor used, experience would suggest taking an excess of bleach liquor and determining the bleach unconsumed in the solution. Most pulps can be treated by adding bleach liquor obtained from good bleaching powder equivalent to 25 per cent. of the weight of wood pulp taken for experiment. In the above case 62·5 c.c. of a good bleaching solution would be equivalent to 2·5 grammes of powder. This figure, as already explained, will vary slightly, but as the value of the solution is determined by means of standard arsenic, the variations can be easily allowed for.

Temperature, etc.—Maintain the water bath at a temperature of 100° Fahr., stirring the mixture occasionally with a glass rod, and testing the solution from time to time with starch iodide paper. When the colour reaches the required standard, filter off the solution and wash the pulp.

A filter paper is not necessary for the purpose of separating the solution, because the pulp, when thrown into a funnel, acts as its own filter. The washing should be continued until the filtrate shows no coloration with starch iodide paper.

Titration of Filtrate.—The amount of unconsumed bleach in the filtrate is determined by means of standard arsenic, and thus the amount of bleach actually consumed by the 10 grammes of pulp accurately determined. The amount of powder used for the bleaching of the pulp is then a matter of calculation.

Checking the Result.—If the amount of bleach originally added proves to be much in excess of that actually consumed, carry out a second test, using bleach liquor containing a slight excess above the equivalent of bleaching powder shown by the first experiment.

In all experiments of this kind it is advisable simply to use only a slight excess of powder, and if the appearance of the wood pulp gives some clue as to the probable amount of bleach, the first experiment will frequently give the desired result without a check test.

Sample Sheets of Bleached Pulp.—By means of a small hand mould make up a few sheets from the bleached pulp, in order to have a permanent record of the colour produced under the conditions of the experiment. Attach these sheets together with one or two pieces of the original pulp to the certificate.

Recording the Colour of Pulp.—It sometimes happens that with a series of pulps bleached under similar conditions the sheets vary but little in colour. Such small differences point to the necessity of a method of recording colour more correct than comparative verbal descriptions. Exact records are those of colour analysis by means of the Tintometer. The following experiment may be quoted as an example :—

Three varieties of sulphite pulp were examined, and small sheets were made up from the three samples as follows :—

(1) Sheets of the original unbleached pulp.

(2) Sheets from the pulp after being bleached with 10 per cent. of bleaching powder.

(3) Sheets of the pulp after treatment with 18 per cent. of the powder.

The colour analysis of the samples is given in a table.

These results are interesting and instructive, as showing the gradual elimination of the non-cellulose constituents of the pulp and the exact changes in colour due to the varying extent of bleaching or oxidising action. The stages of colour are represented by the combinations of the standard glasses used. In the original pulp we have the combinations of red, yellow and blue; in the pulp bleached with 10 per cent., red and yellow only, and in the final product some traces of yellow. This table (see next page) is the more interesting because the gradual elimination of the colouring matter is expressed in numerical terms.

The significance of the colour readings is naturally only familiar to those who are constantly handling the Tintometer instrument. When an observer has become accustomed to the depth of colour of the various standard glasses, then the numerical expression conveys an accurate idea of the colour, so that after some practice he obtains a mental picture of the colour of the pulp from the figures which record the visual colour.

Substances examined.	Light brighte than standard.	Standard glasses used.			Visual colour.		
		Red.	Yellow.	Blue.			
Original pulp—					Black.	Orange.	Yellow.
Sample 1 .		1·6	1·65	·76	·76	·84	·05
,, 2 .		1·3	1·4	·70	·70	·60	·10
							Red.
,, 3 .		1·55	1·5	·95	·95	·55	·05
Pulp bleached with 10 per cent.—						Orange.	Yellow.
Sample 1 .		·17	·60			·17	·43
,, 2 .		·15	·58			·15	·43
,, 3 .		·26	·70			·26	·44
Pulp bleached with 18 per cent.—						Green.	Yellow.
Sample 1 .			·26	·01		·01	·25
,, 2 .			·30				·30
,, 3 .			·32				·32

Electrolytic Bleaching.

This term, in its stricter and more correct sense, implies a process in which a bleach liquor prepared by electrolytic methods, is used as a substitute for the calcium hypochlorite solution obtained by treating ordinary bleaching powder with water. In practice this resolves itself into the use of a sodium hypochlorite solution prepared direct from common salt by electrolysis.

In a wider sense the term may also be applied to the use of bleaching powder which has been manufactured from chlorine obtained electrically from salt. In this case the process is only an indirect "electrolytic bleaching," since the actual bleaching agent is still ordinary chloride of lime.

In their relation to the bleaching of wood pulp both systems need to be considered, since there might be certain advantages with the indirect electrolytic treatment in factories favourably situated.

In the first system a solution of common salt is submitted to the action of an electric current, which decomposes the sodium chloride and ultimately produces two substances, caustic soda and chlorine. These products interact in the solution to form sodium hypochlorite, which is then at once available for bleaching. Only a small proportion of the salt is actually converted into the active hypochlorite, and the process depends for its commercial success on a supply of cheap salt and electrical power.

In the second system a solution of common salt is also submitted to electrolysis, but the resultant products of decomposition are carefully separated, and not allowed to combine. The caustic soda is drawn off continuously and subsequently concentrated, while the chlorine gas is taken off and brought into contact with dry lime for the manufacture of bleaching powder, or passed at once into milk of lime and thus converted direct into bleach solution. Complete decomposition of the original salt is effected by this means, and two products of commercial value are obtained. In pulp factories where wood is treated by the soda process the use of this second system might be a decided advantage.

The process of electrolysis presents no difficulties in the laboratory, but the practical application of them for the purpose of devising a commercial and remunerative system for the manufacture of alkali and chlorine has proved a difficult and costly task.

The laws of electrolysis, together with the terms and nomenclature expressing the relations of current to chemical work, are mainly due to Faraday. In regard to the electrolysis of common salt a current of one ampere passing through a solution of the sodium chloride will liberate 1·32 grammes of chlorine per hour and the equivalent quantity of caustic soda simultaneously.

The terms usually employed in reactions relating to electrolysis are as follows:

Ampere.—The unit of current or rate of flow in terms of coulombs per second (*infra*).

Volt.—The unit of electromotive force, or electrical pressure, which applied to a conductor having a resistance of one *ohm*, will give a current of one ampere.

Ohm.—The unit of resistance, which is that of a uniform column of mercury 106·3 cm. long, and mass equal to 14·45 grms.

Coulomb.—The unit of quantity, or the quantity of electricity derived from a current of one *ampere* in one second.

Watt.—The unit of power is the power of a current of one ampere flowing under a pressure of one volt. It is equal to one *joule* per second.

Joule.—The unit of work, or the energy expended in one second by a current of one *ampere* passing through a resistance of one *ohm*.

Electrolysis.—The chemical change of decomposition produced by a current of electricity passing through a solution of a substance.

Electrolyte.—A term applied to the solution undergoing electrolysis.

Electrode.—The terminal conductor, usually carbon or a metal, by means of which the current is passed into or taken away from the solution undergoing electrolysis.

Anode.—The conductor or electrode which conducts the current into the solution or electrolyte.

Cathode.—The conductor or electrode which conducts the current out of the solution or electrolyte.

Anion.—The product of electrolysis obtained from the electrolyte which is given off at the anode, and is always electro-negative in character.

Cation.—The product of electrolysis obtained from the electrolyte which is given off at the cathode, and is always electro-positive in character.

Power Consumption.—This is usually measured in "kilowatts."

A watt = ampere × volt.
A kilowatt = 1,000 (amperes × volts).
746 watts = 1 horse-power.

Production of active chlorine.—The equivalent of one ampere passing through a solution of salt is 1·32 grammes of chlorine per hour (at the anode). In practice a smaller yield is obtained owing to secondary reactions and equivalent loss of current efficiency, increasing as the amount of "active chlorine" accumulates. The actual mean production is about one gramme of chlorine per ampere-hour for weak liquors. On this basis with a potential of 3·5 volts,

For 1 gramme chlorine = 1 ampere-hour.
1 kilo chlorine = 1,000 ampere-hours.
1016 kilos chlorine = (1,000 × 1,016 × 3·5) watts.

or 1 ton chlorine = 3,556,000 watts.
= 3,556 kilowatts.

The actual consumption of power under the systems now in practical use appears to be 5,000 kilowatts for a ton of "active chlorine."

The earliest attempts at the direct industrial production of bleach liquor, *i.e.* a solution of a hypochlorite, were made by E. Hermite over twenty years ago. On this system the electrolyte was a solution of Magnesium Chloride (2—3 per cent. $MgCl_2$), which was electrolysed to a concentration of about 3 grammes "chlorine" per litre.

An essential feature of this process was the continuous circulation of the electrolysed liquor as between the electrolyser and the beating engine, and the realisation of the cycle of changes, viz:—the electrolysis of the magnesium chloride to hypochlorite in the electrolyser and its reversal in the beating engine as the result of chemical work done. The Hermite system on this principle was found unworkable, for, owing to secondary reactions and waste consumption of bleaching compounds, the percentage current efficiency was very low. It is still used, however, as a method of producing a hypochlorite solution.

There are now several types of electrolytic apparatus in use, based on the conversion of salt (sodium chloride) into sodium hypochlorite.

Haas and Oettel Apparatus.—This electrolyser is simple in construction and working, and is in considerable favour where small quantities of bleach liquor are required, particularly in laundries and textile works. It consists of a narrow earthenware vessel containing the electrodes, which are so arranged that the vessel is divided into a number of separate compartments, provided with a feed pipe to each near the bottom, and an overflow channel at the top. This vessel is immersed in the large store tank containing a salt solution of 10° Be. When the current passes, the hydrogen gas liberated at the cathode causes the solution to froth and rise up in each compartment. This produces an automatic continuous circulation of the electrolyte solution, since the expulsion of some of the latter through the overflow pipes produces a partial vacuum in each chamber, which causes fresh liquor to pass into the chambers through the feed pipes at the bottom.

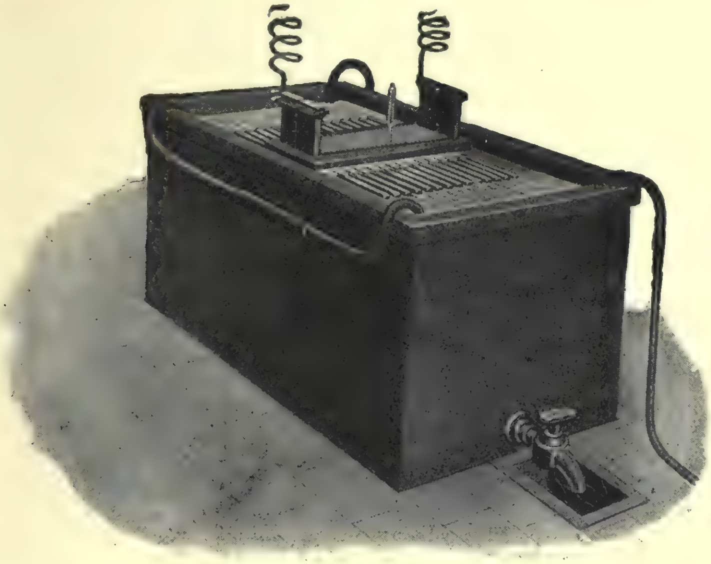


FIG. 20.—Haas and Oettel Electrolyser.

Adequate arrangements of cooling pipes ensure a comparatively low temperature in the cell, which is essential to the production of a maximum amount of hypochlorite and a minimum amount of chlorate.

The current is maintained until the desired strength of "active chlorine" has been obtained, at which point the charge is drawn off into store tanks, and a fresh quantity of salt pumped into the apparatus. The process is therefore intermittent.

The standard pattern for the production of large quantities of sodium hypochlorite as required in the paper-mill is shown in Fig. 20.

It is constructed wholly of stoneware, the electrodes are made of "carbon," and the apparatus is adapted for a continuous current at 110 volts. The makers quote the following figures as indicating its output and economy of working, based on a 12 hours test:—

Capacity of Tank	750 litres = 166 gallons.
Salt used.	280 lbs. = 166 gallons at 23° Tw.
Temperature of solution	20° C.
Current	43 amperes.
Potential	110 volts.
Chlorine obtained	26·73 lbs.

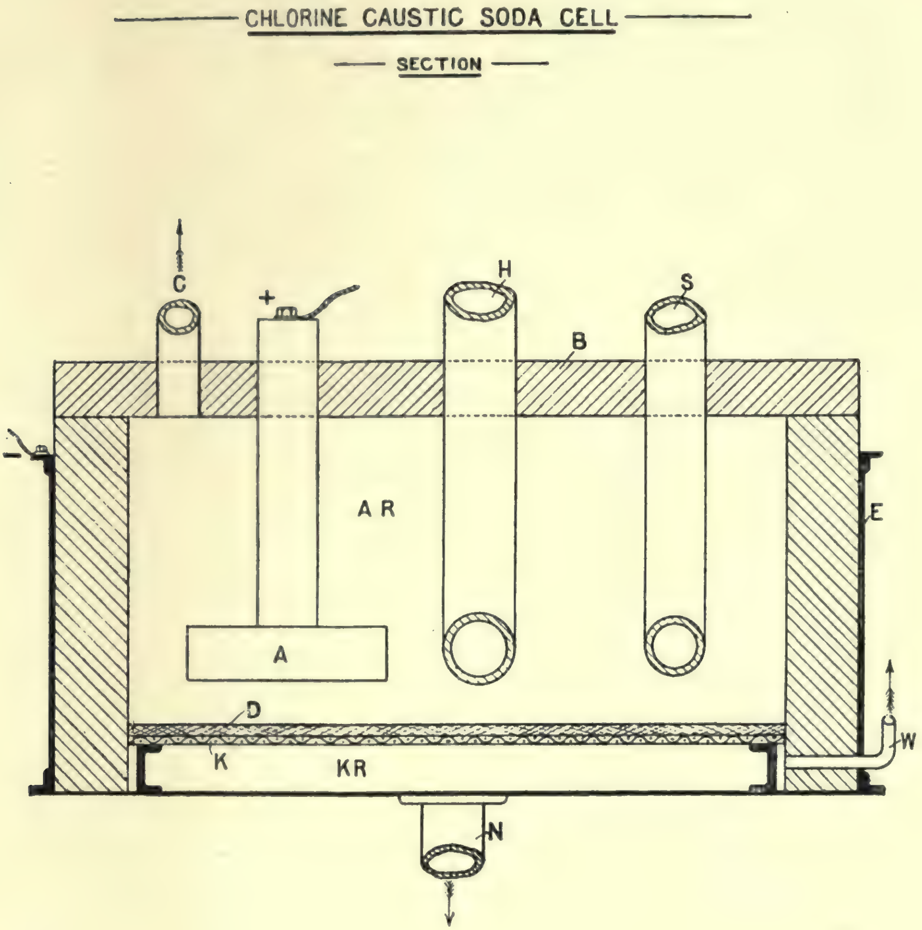
With these results the figures for the production of one ton of active chlorine are:—

One cell produces in one working day 53·0 lbs. chlorine.

Power required $\frac{110 \times 43 \times 24}{1{,}000} = 113{\cdot}6$ kilowatt hours.

One ton chlorine requires power = 4,800 kilowatt hours.
and salt = 10·5 tons.

Siemens and Halske Electrolyser.—This apparatus is already in use in several paper-mills, notably the Borregaard works of the Kellner-Partington Co. in Norway. The electrodes are made of platinum-iridium gauze arranged horizontally in shallow stoneware electrolysers, or in



A	CARBON ANODE	H	HEATING PIPE
A R	ANODE CHAMBER.	K	IRON WIRE NET, CATHODE
B	CONCRETE COVER.	K R	CATHODE CHAMBER
C	CHLORINE OUTLET	N	CAUSTIC SODA OUTLET.
D	DIAPHRAM CLOTH.	S	SALT INLET
E	IRON BATH	W	HYDROGEN OUTLET.

FIG. 21.

iron vessels suitably lined with glass or other insulating material. These vessels are so constructed as to form a series of small independent decomposing cells, and the solution of salt is passed continuously through the whole series. The electrodes are connected up so that no electrical connections inside the several electrolysers are necessary. The bleaching liquor produced is drawn off into reservoirs, or kept in circulation until the "active chlorine" is at the working strength.

The makers[1] of this apparatus have published interesting statistics from time to time and give the following particulars in reference to some works in Switzerland.

At this mill the quantity of bleach liquor obtained in 12 hours amounts to 2,300 litres containing 15 grammes of active chlorine per litre.

Current used = 120 amperes at 120 volts.
Salt consumed = 250 kilos in 2,300 litres of water to give 15 grammes chlorine per litre.

Working out the cost of production with the above figures the results are :—

$$\text{Chlorine produced } \frac{2,300 \times 15}{1,000} = 34{\cdot}5 \text{ kilos.}$$

$$\text{Electrical power } = \frac{120 \times 120 \times 12}{1,000} = 173 \text{ k.w. hours.}$$

$$\left.\begin{array}{l}\text{Electrical power for 1,016 kilos}\\ \quad\text{chlorine . . . .}\end{array}\right\} = \frac{173 \times 1,016}{34{\cdot}5} \text{ k.w. hours.}$$

Electrical power for 1 ton chlorine = 5,090 k.w. hours.

Salt for 34·5 kilos chlorine = 250 kilos.
,, ,, 1,016 kilos chlorine = 7,500 kilos.
,, ,, 1 ton chlorine = 7·5 tons salt.

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[1] "Papermaker's Monthly Journal," May, 1910.

The following table has been given to show the cost of power and salt for one kilogram active Chlorine.

No.	Price per litre.	Cost of power for 1 kg. active chlorine.	Cost of salt for 1 kg. active chlorine.	Cost of power and salt for 1 kg. active chlorine.
	s. d.	d.	d.	d.
1	1 4	1·42	0·72	2·14
	1 2	2·85	0·72	3·37
	0 1	5·7	0·72	6·42
2	1 4	1·3	0·864	2·164
	1 2	2·6	0·864	3·464
	0 1	5·2	0·864	6·064
3	1 4	1·2	1·08	2·28
	1 2	2·4	1·08	3·48
	0 1	4·8	1·08	5·88
4	1 4	1·15	1·44	2·59
	1 2	2·30	1·44	3·74
	0 1	4·60	1·44	6·04

The Siemens and Halske apparatus is so constructed that the products of electrolysis, namely chlorine gas and caustic soda, can be separated continuously during electrolysis, and when so desired caused to interact outside the electrolyser for the production of bleach liquor direct. The makers claim that by this means the same amount of active chlorine can be produced with lesser power and with a smaller proportion of salt, and state that the power consumption is 3·5 to 4 k.w. hours for each one pound of active chlorine. It is obvious that a plant capable of producing bleach and soda in this way possesses many advantages over those forms of apparatus in which only bleach liquor is produced. In localities where lime is plentiful and cheap, and where caustic soda finds a ready market, the Siemens and Halske electrolyser should give economical results. Taking the figures above quoted with the apparatus utilised only for the manufacture of bleach liquor, the cost of one ton of active chlorine would appear to be as follows:—

	Quantities.	Price.	Total. £ s. d.
Power . . .	5,090 k.w. hours	at ¼d. per unit[1]	5 6 0
Salt . . .	7·5 tons	at 12s.	4 10 0
Renewals . .	—	say	0 10 0
Interest and other charges . .	—	say	1 0 0
			£11 6 0

[1] The unit is a kilowatt hour.

Schuckert's Electrolyser.—This apparatus consists of cells similar to those employed in other electrolysers, the chief feature being the special form of the electrodes. In the Siemens and Halske apparatus the electrodes are constructed of platinum and iridium, while in the Haas and Oettel they are provided with electrodes made entirely of graphite. In Schuckert's electrolysers the positive electrodes are made of platinum and the negative electrodes of graphite. This arrangement is based upon the fact that the carbon electrode is not attacked by the electro-positive element at the negative pole, and the platinum is not acted upon by the electro-negative compounds present at the positive pole. Several advantages are claimed for this arrangement, as not only does the apparatus require less frequent renewels, but the presence of smaller particles of carbon in the liquid is avoided. This electrolyser appears to be capable of providing strong solutions of bleaching liquid. With a 10 per cent. solution of salt a bleaching liquid containing 15 grammes of active chlorine per litre can be obtained with an energy consumption of 3·2 kilowatt hours and a supply of 5·4 lbs. of salt per lb. of chlorine. The usual limit is 20 to 22 grammes of active chlorine to the litre, and with a Schuckert electrolyser 30 to 35 grammes per litre can be obtained.

Some interesting experiments have been made by Dr. Fraass with electrolytic bleach liquor prepared by the Schuckert apparatus.[1]

The cellulose examined was easy bleaching sulphite pulp. A weighed quantity of the pulp was mixed with water and a definite proportion of bleach liquor (*a*) from chloride of lime and (*b*) from electrolytic bleach liquor. The temperature of the operation was maintained at about 30° C. until the whole of the chlorine had been consumed. The results of this test are given as follows :—

COMPARISON OF BLEACHING EFFECTS OF (*a*) CHLORIDE OF LIME AND (*b*) ELECTROLYTIC LYE.

Test No.	Pulp concentration.	Active chlorine present. Grammes per litre.		Chlorine used per 100 grammes of air-dried pulp.		Resulting white.
		a	*b*	*a*	*b*	
1	1:15	0·67	0·67	2·00	2·00	Same with both.
2	1:16	1·25	1·25	1·99	1·99	Better with electrolytic lye.
3	1:12·7	0·80	0·80	2·00	2·00	,,
4	1:12·5	0·73	0·73	1·82	1·82	,,
5	1:12·5	0·80	0·80	2·02	2·02	,,
6	1:12·7	0·80	0·80	2·00	2·00	,,
7	1:12·7	0·79	0·79	2·00	2·00	,,
8	1:20	1·00	1·00	2·00	2·00	,,
9	1:20	1·50	1·50	3·00	3·00	,,
10	1:20	1·00	1·00	2·00	2·00	,,
11	1:20	1·00	1·00	2·00	2·00	,,
12	1:20	1·50	1·50	3·00	3·00	,,

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[1] For further details see "Papier Fabrikant," 1909.

Further experiments were made by Dr. Fraass to determine the actual saving of chlorine, if any, effected by the use of electrolytic chlorine. The following results were obtained.

(*a*) Refers to Chloride of Lime; (*b*) Refers to Electrolytic Lye.

Test No.	Pulp concentration.	Active Chlorine present. Grammes per litre.		Chlorine used per 100 grammes of air-dried pulp.		Resulting save with *b* in per cent. Chlorine.	Better white with.
		a	*b*	*a*	*b*		
14	1:20	1·01	0·995	2·02	1·99	1·43	*b*.
16	1:20	3·00	2·99	5·50	5·40	1·90	*b*.
18	1:15	1·27	1·23	2·06	2·00	2·90	*b*.
20	1:16	1·29	1·24	2·06	1·99	3·40	*b*.
22	1:20	2·27	2·17	4·54	4·34	4·40	*b*.
24	1:20	2·27	2·15	4·54	4·30	5·26	*a* and *b* same.
26	1:12·5	0·89	0·80	2·21	2·00	10·0	*a*.
28	1:20	1·00	0·90	2·00	1·80	10·0	*a*.
30	1:12·7	0·80	0·71	2·00	1·80	10·0	*a*.

From the foregoing brief account of electrolytic bleaching systems it would appear that evolution on the basis of experience has limited these systems to the production of a solution of a hypochlorite which is used upon the pulp or cellulose textile to be bleached, and is then rejected as a waste liquor after the bleaching agents are exhausted in doing chemical work upon the pulp or fabric.

The idea of an industrial cycle as advanced by Hermite is rendered impossible by the fact, which is too often overlooked, that with the bleaching or oxidising action there are secondary reactions, as a result of which organic products pass into solution. These products will consume oxygen until reduced to compounds of the lowest molecular weight. This of course is entirely waste work.

The electrolytic systems finally evolved are therefore intermittent, and the rejection of the waste solution involves a loss of so much salt which is too dilute a form to be usefully recovered.

When we come to the question of the direct production of caustic soda and chlorine, we arrive in the region of "heavy" chemical industry.

As a result of inventive evolution there are two systems finally established in this country, which are those of Castner-Kellner, and Hargreaves-Bird.

Each of these systems produces chlorine as such, which is converted into bleaching powder, or bleaching liquor, as an ordinary chemical operation outside the electrolytic system.

As regards the work of the cathode, or soda end of the process, the Castner-Kellner system produces caustic soda owing to the special disposition of its electrode, whilst in the Hargreaves-Bird process the soda which is produced as caustic soda is removed in the form of carbonate.

These well-established systems, for the production of alkali and "bleach," are not easily engineered, and they are in many respects unsuitable for small production.

The matter with its technical and commercial issues is much too complicated to be usefully discussed within the scope of this work.

Many problems are presented which are as yet by no means solved and it is quite possible that the over-production of chlorine, which is an incidental feature of these systems, may lead to further developments of the industrial production of cellulose on very different lines from those which are exploited to-day as almost stereotyped.

Imports of Wood Pulp into Great Britain, 1904—1908.

(From the Annual Statement of Trade of the United Kingdom).

	Quantities.				
	1904.	1905.	1906.	1907.	1908.
Chemical, Dry.	Tons.	Tons.	Tons.	Tons.	Tons.
From Russia	9,533	12,179	11,698	13,558	15,501
,, Sweden	131,655	133,564	127,046	157,916	163,074
,, Norway	55,213	63,948	77,047	70,957	77,665
,, Germany	5,609	7,186	7,584	15,514	23,687
,, Netherlands	2,781	2,622	2,595	3,280	1,820
,, Portugal	2,115	2,482	2,219	2,416	2,170
,, Austria Hungary . .	2,183	3,163	1,765	4,305	1,876
,, United States of America	1,188	2,917	2,691	1,942	855
,, Other Foreign Countries	862	349	707	300	212
Total from Foreign Countries	211,139	228,410	233,352	270,188	286,860
Total from British Possessions	253	2,964	7,297	753	1,795
Total	211,392	231,374	240,649	270,941	288,655
Chemical, Wet.	Tons.	Tons.	Tons.	Tons.	Tons.
From Sweden	7,112	6,948	7,261	13,295	16,310
,, Norway	17,673	11,117	9,109	8,724	10,976
,, Other Foreign Countries	. .	10	. .	45	10
Total from Foreign Countries	24,785	18,075	16,370	22,064	27,296
Total from British Possessions (Canada)	. .	19	. .	250	. .
Total	24,785	18,094	16,370	22,314	27,296
Mechanical, Dry.	Tons.	Tons.	Tons.	Tons.	Tons.
From Russia	3,199	2,776	1,999	1,037	2,061
,, Sweden	2,984	3,922	1,936	2,428	3,810
,, Norway	2,811	3,553	2,733	2,593	2,192
,, Other Foreign Countries	154	16	1	11	10
Total from Foreign Countries	9,148	10,267	6,669	6,069	8,073
Total from British Possessions (Canada)	51	. .	. .	. .	1,453
Total	9,199	10,267	6,669	6,069	9,526

	QUANTITIES.				
	1904.	1905.	1906.	1907.	1908.
MECHANICAL, WET.	Tons.	Tons.	Tons.	Tons.	Tons.
From Russia	5,452	2,614	1,686	2,899	2,608
,, Sweden	30,741	32,940	31,212	43,610	46,019
,, Norway	224,620	202,249	229,202	262,256	277,988
,, Germany . . .	25	25	. .	645	799
,, Other Foreign Countries	74	182	64	220	. .
Total from Foreign Countries	260,912	238,010	262,164	309,630	327,414
From Canada	62,957	80,236	80,959	63,545	95,543
,, Other British Possessions	. .	31	. .	. .	. .
Total from British Possessions	62,957	80,267	80,959	63,545	95,543
Total	323,869	318,277	343,123	373,175	422,957

CHAPTER VI

NEWS AND PRINTINGS.

THE applications of wood pulp, though large and of first-rate industrial importance, are not numerous. Its utilisation, however, in paper-making is essentially one of great influence, and in point of fact this industry at the present time dominates the wood pulp market. In this country there have been several well-marked phases of expansion of the industry. A prominent landmark was the repeal of the duties on paper in 1860. By a coincidence this indirect condition of expansion synchronises with the introduction of esparto grass to develop rapidly into an important staple raw material, almost a generation in advance of the wood pulp age. By the year 1880 the importation of esparto had reached 200,000 tons, and it is a somewhat remarkable feature of this industry that the consumption of esparto has shown no growth from this figure.

The wood pulps have been independently developed. "Mechanical" wood pulp or ground wood dates back to the period 1850—60. The chemical pulps in this country were pioneered by C. B. Ekman in collaboration with George Fry in the period 1870—80. This early venture was capitalised by Thomson, Bonar & Co., and worked at Bergvik, Sweden, and Ilford, Essex. The new industry attracted other pioneer workers, notably E. Partington in this country, and C. Kellner in Austria, who individually and jointly did much to establish the new order during the following decade. It requires a little calculation to estimate the growth of the industry during this period, 1880—90, since the statistics of importation, in the Board of Trade returns, are a complex return including "Esparto and other Materials": it was not until 1888 that the returns of wood pulp importation were separately recorded. The growth of the wood pulp trade from 1880 to 1888 represents an estimated quantity of 100,000 tons, and at this later date the industry had become widespread and firmly established in Scandinavia, Germany and America. The English importation has continued to grow, and the figures for the first nine years of the century may be cited :—

The total world's production of "chemical pulp" is fast approaching 3,000,000 tons. In taking this statistical view of the paper industry we may note the figures arrived at by Krawany, for paper consumption per head per annum, in European countries :—

	Kg.		Kg.		Kg.
England	25·3	Belgium	11·1	Russia	2·2
Sweden	24·0	Holland	10·8	Greece	1·8
Finland	22·5	Italy	7·5	Turkey	1·8
Germany	19·7	Denmark	6·4	Roumania	1·4
Norway	16·3	Luxemburg	4·8	Bulgaria	1·3
Switzerland	15·0	Spain	4·4	Bosnia	0·7
France	14·0	Hungary	3·6	Servia	0·6
Austria	11·1	Portugal	3·4		

Another result of this statistical inquiry is the ascertained annual increase of the world's production, which at $5\frac{3}{4}$ per cent. is nearly double the estimated increase of other large manufactures, viz., $2\frac{3}{4}$—$3\frac{1}{2}$ per cent. These figures are taken from an interesting paper by Dr. A. Klein on "Cellulose, Wood Paper, Artificial Silk," recently published (*Chem. Zeit.*, 60, 521—530 (1910)).

The most significant development in the paper-making art and industry founded on wood pulp is in the production of "news," and we may take "News and Printings" as the subject of this chapter, and typical, in fact, of the industrial age we live in.

The enormous quantities of mechanical and chemical pulp manufactured to-day are used chiefly in the production of "news" and cheap printing papers.

A modern newspaper contains about 70 per cent. of mechanical pulp mixed with 30 per cent. of chemical pulp. In addition to the fibrous constituents the paper will also contain about 8 to 10 per cent. of china clay, and a small proportion of rosin size. As far as the paper mill is concerned, the process of manufacture is almost entirely an engineering problem, since all the materials used are purchased largely in a completely manufactured state, the object being to eliminate chemical processes whenever possible.

This is only true of paper mills dependent on outside sources for the supplies of pulp and chemicals, but the tendency of modern practice in such mills is to reduce the question to one of mixing certain ingredients and getting the maximum output of paper at a minimum cost.

At the same time chemistry plays an important part in the efficient and economical working of a "news" mill.

From start to finish every process is controlled by analysis, while improvements in the quality of the paper are gradually introduced, either by the use of superior wood pulps, or by suggestions that arise from a careful study of the systematic records kept.

A general survey of the operations necessary for the production of this class of paper will show the intimate relation between chemistry and engineering in almost any industrial process.

Power.—The amount of coal consumed averages 18—20 cwt. per ton of finished paper. Most of this fuel is required for motive power, though a certain proportion is used in drying the paper during manufacture. The steam engine is employed for this in nearly every paper mill, but in a few cases gas engines worked from gas producers have been tried.

The maintenance of an extensive boiler plant on up-to-date principles demands the control of the coal supplies in the matter of weight received, the analysis of same for moisture, ash left on combustion, and calorific value; the systematic analysis of the waste gases from the boiler flues to prevent careless firing of the boilers, and to ensure complete combustion; the use of suitable water for boiler purposes, involving the utilisation of all condensed steam and hot water, and the adoption of some efficient process for softening any hard water which must be employed in addition.

All these operations are controlled by simple methods of chemical analysis. The theoretical value of a given coal supply having been found by analysis, and expressed in terms of the heat units available, it should be possible to determine what proportion has been expended in useful work, the particular stage in the manufacture of the paper at which each proportion has been utilised, and finally what amount has been wasted. Questions of this kind are of great importance, and involve measurements of many factors.

Chemicals.—From what has been said as to the nature of the operations involved in the manufacture of the modern newspaper, it is evident that the number of chemicals properly so called is not very large. Amongst them will be found rosin and alkali used for sizing, or some form of prepared size; china clay used as a loading; lime for the water-softening process; alum and sundry colouring matters and pigments; acid and bleaching powder; starch, etc.

Oils and greases required for lubricating purposes, and other supplies connected with economical power, also need attention at the hands of the analyst.

Wood Pulp.—The exact control of the supplies of pulp is an important part of the duty of the mill chemist. The determination of the air-dry weight of every consignment of pulp is sometimes regarded as a mechanical and simple task, but it is one of considerable responsibility. All pulps, whether delivered in a dry state or in the moist condition, require to be tested for moisture.

Chemical pulps are tested regularly for quality, particularly as to their behaviour with bleach. Some pulps are very difficult to bleach, and consume a large amount of bleaching powder. In many cases where a white pulp is required a ready bleached pulp is used, but this plan is not economical since it is cheaper to treat the pulp at the paper mill than to buy the material already bleached.

Mechanical pulps vary in quality and freedom from coarse fibre. The differences in bulking qualities are very marked and may be measured in the laboratory on small samples readily.

Paper.—The examination of the finished paper from the machines in regard to its physical properties of strength, bulk, finish and sizing is a matter of routine in a well-ordered mill. The testing of contract samples in respect of actual composition to determine the percentage of loading, the proportions of mechanical and chemical pulps present and the existence of other fibres, as well as the usual physical tests mentioned, is a necessity when making papers to sample.

There are many items in manufacture which call for the exercise of careful and painstaking research on the part of the chemist, and when these technical questions are studied exhaustively by him under the needful encouragement of the authorities, the information gradually accumulated is of the greatest value. The systematic correlation of modifications in manufacture, with the improvements in the finished paper by proper classified records which can always be referred to, is perhaps one of the most important points, but one which is almost neglected in the average mill.

Improvements in the Manufacture of Cheap Newspaper.

During the last twenty-five years great progress has been made in the production of common paper from wood pulps. The contrast between the old and new methods is best illustrated by reference to the output of a machine.

When wood pulp was first used there were few machines capable of making a sheet of paper more than 120 inches wide at a speed of 200 to 250 feet per minute, with an average production of 50 tons per week. To-day the modern machine will produce a sheet of paper 170 inches wide at a speed of 500 feet per minute, with an output of nearly 45 tons per day.

Preparation of the Beaten Pulp.—The proper proportions of mechanical and chemical pulp are first disintegrated by treatment in large potchers or special machinery, being mixed with a suitable quantity of water, or generally with waste waters from the paper machine. The mixture is then transferred to a beating engine capable of holding sufficient wet material to produce one ton or more of dry paper, and beaten for about thirty or forty minutes. This is a process far removed from that which obtains in the treatment of rag, when the beating engine giving the best results is only capable of holding wet stuff equivalent to 1 to 2 cwt. of dry pulp, and the operation is only completed after eight or nine hours.

To the mixture in the engine about 10 per cent. of china clay calculated on the dry weight of pulp is added. Rosin size to the extent of 1 or 2 per cent. is then thoroughly incorporated, and alum added to precipitate the size which adheres to the fibres. The pulp is suitably dyed to the desired colour by means of pigments or soluble aniline colours.

The subject of the beating of pulp is one of great technical importance, since the quality and characteristics of a paper are easily altered by modifications in the process of beating. In an elementary treatise of this kind it is impossible to enter fully into the question, and only a brief indication can be given of the variations which are obtained as a matter of daily routine.

The main object of the beating process is the proper isolation and reduction of the individual fibres after the raw material has been sufficiently boiled and bleached. There are many types of machines available for the purpose, but all constructed on the same principle, namely, the circulation of the mass of pulp and water in a narrow trough provided with a revolving beater roll which, as it rotates, acts upon the mass drawn between the knives of the roll and a set of knives fixed on the bottom of the trough.

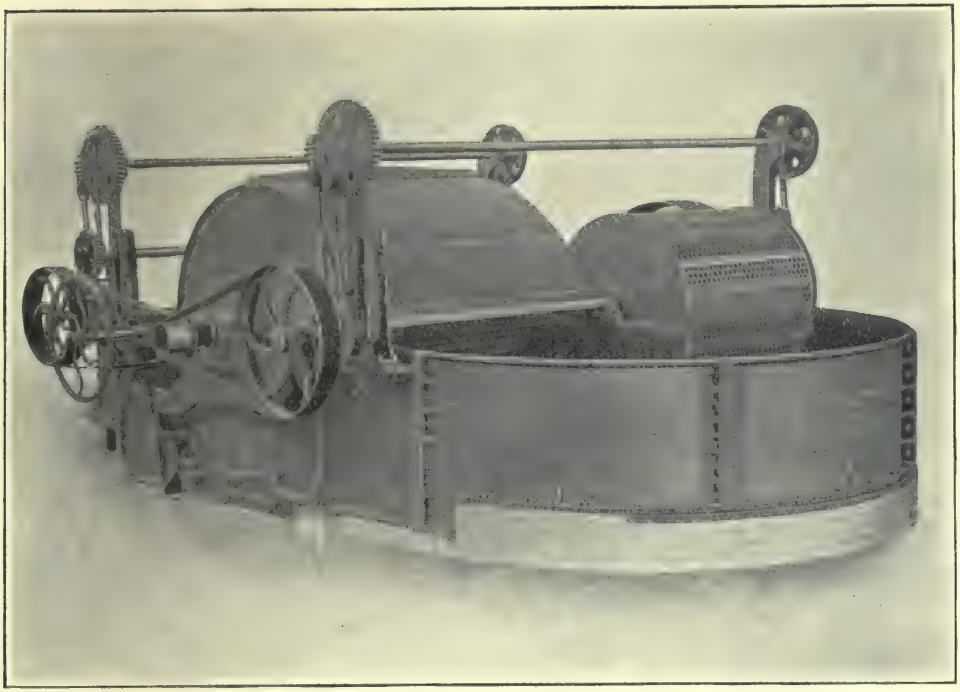

Fig. 22.—The "Hollander" Beating Engine.

The general construction of an ordinary "Hollander" beater is shown in the diagram. The engine consists of an oval-shaped vessel divided into two channels by a "mid-feather" or partition fixed along the centre of the vessel, but not extending completely to the ends. In this way the oval vessel is divided into two channels. An adjustable beater roll, which is a solid cylindrical drum fitted with knives projecting from its surface, rotates in one of the channels and revolves above a set of knives projecting from the bottom of the trough. The engine is filled with the required amount of pulp and water, and by the rapid rotation of the beater roll the mixture is constantly circulated round the troughs of the engine and passes continuously between the knives on the beater roll and those which are stationary. The fibres are thus completely separated and gradually reduced.

The varied effects produced in beating wood pulps may be illustrated by one or two examples. Thus, if soda pulp is beaten quickly with sharp knives, the beater roll being close down on to the stationary knives, then a soft spongy paper resembling blottings is produced. If on the other hand, a strong sulphite pulp is beaten slowly for a long time—eight or nine hours—the knives being blunt, and the beater roll being lowered gradually during the process, then a close dense sheet of paper, strong and resembling parchment, is obtained. In the latter case the curious assimilation of water by the fibre takes place, with a production of an imitation parchment paper.

Probably the beating operation is the most important in the various stages of the manufacture of paper, on account of the great variations which are possible by altering the conditions under which the pulp is beaten.

It is customary in mills where the ordinary type of "Hollander" is used to pass the beaten stuff through a refiner, whereby the fibres, which are more or less interlocked by the beating, are brushed out. The types of refiners mostly used in this country are the "Marshall" and the "Jordan."

The Fourdrinier Paper Machine.—The pulp after beating is ready for conversion into paper. It is discharged from the beating or refining engines into large reservoirs or stuff chests, of which there are two to each paper machine. The contents of one chest are supplied to the machine while the second is being filled from the beaters, so that the pulp is uniform and ensures the manufacture of a regular sheet of even weight and thickness.

The pulp flows through a number of strainers which serve to retain any coarse pieces of pulp and other impurities. For the fast-running news machine the strainer is a hollow circular drum, the shell of which consists of a series of curved brass plates bolted together, each scored with fine slits. The drums revolve slowly and are kept in a state of violent agitation, so that the fine pulp passes through the slits and the coarse material is retained. The mixture of pulp and water flows in a continuous stream on to the surface of an endless "wire." This consists of a wide band of wire gauze stretched horizontally over two rolls, known technically as the "breast roll" and "couch roll." The stream of pulp is carried forward at a rapid pace, the water finding its way through the meshes of the wire, and the fibres settle down on the surface of the wire cloth interlacing or "felting" with one another. Further quantities of water are removed from the pulp by vacuum strainers or boxes fixed under the wire near the couch roll, and the "web" of paper then passes between the couch rolls which compress the fibres, remove a certain proportion of water, and give firmness to the sheet of wet paper.

The most recent innovations which have been introduced to facilitate an increased output of paper and at the same time an improvement in the strength of the sheet, have for their object devices for increasing the speed of the paper machine. Amongst these may be mentioned the "Eibel" method of manipulating the machine wire. Under this system the wire cloth upon which the pulp flows is inclined at a considerable angle from the breast roll to the couch roll so that the material flows downhill, so to speak. By this simple device it is possible to obtain a rapid flow of a very dilute mixture of pulp containing large quantities of water, which latter is easily removed owing to the slope of the wire cloth. Another improvement is the substitution of a vacuum couch roll in place of the ordinary solid roll hitherto employed, thus obviating the use of a top couch roll. The wet sheet of paper passes over a large roll, part of the surface of which as it revolves is submitted to the action of a powerful vacuum, so that the excess of water is removed from the wet sheet of paper. The fibres are felted together and the life of the wire cloth is prolonged. The web leaving the couch rolls is drawn through two or more sets of press rolls, which serve to compress the fibres into a firm adherent sheet.

The wet sheet of paper then passes over a number of drying cylinders, which are heated internally with steam. In the earlier machines eighteen to twenty such cylinders amply provided all the drying surface necessary, but in the modern paper machine thirty-two to thirty-six cylinders are required to dry the paper completely, owing to the largely increased output.

The drying of the paper is an important item, because it is desirable to dry the paper as slowly as possible at a comparatively low temperature. When the number of cylinders is limited, a much higher temperature is necessary to ensure complete drying of the paper, but in such case, while the output of finished paper can be maintained, the strength of the sheet is seriously diminished.

The paper is afterwards passed through calenders in order that a surface or finish may be imparted to it. The ordinary calenders fixed at the end of a machine used for the manufacture of news consist of a number of highly polished chilled rolls, and the paper in passing over and under these rolls is further compressed and at the same time glazed.

No further process is necessary for ordinary news, but the reels of paper produced at the end of the machine are re-reeled and cut into the required lengths and sizes.

CHAPTER VII

WOOD PULP BOARDS

Large quantities of mechanical wood pulp are used for the manufacture of pulp boards which have many industrial uses such as for boxes, packing cases, cards, calendars, advertisement goods, picnic dishes and a variety of similar articles.

In some cases the pulp is mixed with stronger fibrous material such as jute, hemp, and chemical wood pulp, particularly for boxes of high quality which are required to withstand rough usage. The heavy stout boards frequently used for railway carriage panels are made from the best materials and by hand or manual process, the sheets being produced on moulds similar to those employed in the manufacture of hand-made papers.

The cheapest qualities of thin boards, of which an ordinary tram-car ticket is a typical example, are produced on the continuous-board machine, which in general construction resembles the ordinary Fourdrinier or paper machine.

For certain grades of pulp boards which cannot be made on the continuous-board machine, on account of the thickness, a simpler form known as the single-board machine is used.

The chief advantage of a wood-pulp board as contrasted with the common strawboard, which it has superseded to a large extent, are to be found in its more attractive appearance, its cleanliness, and above all its bulk, being thick and of light weight. Moreover it has less tendency to crack when folded or bent, and when covered with coloured paper, the colour does not fade as frequently happens with strawboards which have not been carefully made. The traces of alkali often present in common strawboard produce a decided fading of some aniline dyes.

Single-board Machine.—Mechanical wood-pulp boards of any desired thickness are produced in sheets of definite size on this machine. It differs very little from the wet press used in the manufacture of wood pulp itself, and only a brief note of its construction need be given.

The pulp mixed with the requisite volume of water is passed over strainers which remove coarse chips, and pumped continuously into a large wooden vat, containing a hollow cylindrical drum revolving at a slow rate.

The surface of the drum consists of fine wire gauze, and as the drum revolves, the pulp adheres to the surface in a regular and uniform layer or skin, while the water passes freely through the meshes of the wire. The layer of pulp comes into contact, as it passes out of the water, with a travelling felt, and adhering to this, is carried away from the vat and drawn between two heavy rollers, which squeeze out the excess moisture. As the thin sheet of pulp is wound up on the upper roller, it forms a sheet of mechanical pulp which gradually increases in thickness, and when the desired thickness has been reached the sheet is immediately cut away from the roller and put aside. The travelling felt passes round the lower roller and back to the vat containing the mixture of pulp and water.

The process is continuous, and the sheets obtained are then submitted to pressure, thick felts being interposed between the sheets of pulp so that the water drains away completely. The material in this condition then contains about 50 per cent. of dry pulp and 50 per cent. moisture. The sheets are dried, glazed, and cut to any required size, the final thickness of the boards being determined by the pressure applied during the process of glazing.

Continuous-board Machine. —This is a combination of the single-board machine and the ordinary paper-making machine, and is used for making "duplex" and "triplex" papers. The beaten pulp is formed into thin sheets in two or more vats, and these sheets are brought together between rollers so as to produce one sheet of the required thickness. The board then passes over a large number of steam-heated cylinders, and completely dried. The dry board is also glazed and finished by calenders fixed at the end of the machine, and finally cut up into sheets.

No further operations are necessary, the finished board being manufactured and completed by the one machine, the processes following one another automatically.

Machines of this kind are frequently fitted with more than two vats, and in such cases some of the vats are filled with common waste material, while two are filled with a high-class well-bleached pulp. In this way, a good board can be produced cheaply, consisting of a low-grade *middle*, covered on either side with a paper of good quality. The colour of the outer surfaces of the board can be varied.

Box-making.

The great demand for boxes as a convenient substitute for brown paper in the wrapping and packing up of goods has resulted in the creation of an important industry.

Raw Materials.—The boxes are manufactured from strawboards, wood-pulp boards, and "leather" boards. The nature of the composition of the raw material may generally be gathered from the descriptions applied, though the term "leather boards" is somewhat misleading. Many of the so-called boards are made from various kinds of specially prepared wood pulp, but in some cases a small proportion of leather clippings is incorporated with vegetable fibres by suitable treatment.

The cheap flimsy folding boxes used for wrapping medicine bottles and similar temporary purposes are made from common board which contains little more than waste paper. The boards are brittle and do not stand much folding. The leather boards, on the other hand, are wonderfully strong and tough, capable of being bent and twisted into all kinds of shapes.

Classification.—The different kinds of boxes made in large quantities from the raw materials described may be classified as follows:—

(1.) Plain square-shaped boxes, with corners pasted, and finished off with plain or ornamental paper.

(2.) Square-shaped boxes, corners wire stitched.

(3.) Square-shaped boxes, with metal-edged corners.

(4.) Folding boxes.

(5.) Round boxes, made up or stamped.

(6.) Tubes and small cylindrical cases.

Plain Board Boxes.—The boards are first cut into convenient sizes, on an ordinary cutting table worked by hand, or in a rotary millboard cutting machine worked by power. In the rotary machine a large board can be cut up into a number of strips of the required length by means of circular knives fitted on to the shaft of the machine, which knives can be adjusted to any desired degree of accuracy. The strips obtained from the cutter are afterwards reduced to the required width.

The square pieces of board are next *scored,* that is to say, slight cuts are made on the board where the sides are bent up to form a box. If the pieces of board are not scored in this way they crack and break when bent into the form of a box. Machines are also employed in which the cutting and scoring are carried out simultaneously.

After the boards have been scored the corners are cut out by simple stamping machines and the box at once made up. The operator bends over two edges of the board to form a right angle, and places the corner thus formed in a stamping press which presses down a small piece of gummed paper of the proper length round the corner fastening the two edges together. This operation is repeated four times in the making of the boxes. The lid of the box is manufactured in a similar manner, due allowance being made in the cutting of the board in order to obtain a well-fitting lid.

The boxes are left plain, or finished off with printed labels and ornamental paper.

The covering of boxes with ornamental paper is a simple process, the variations being not so much in the methods employed as in the materials used. Most of the boxes used by drapers are generally covered with a flint-glazed box paper, the edges of the boxes being finished off with coloured paper of a similar character. The edges of the boxes are first covered with thin strips of paper either by hand or by machinery, the top and sides of the box being afterwards covered with the white glazed paper in such a manner as to leave the coloured edges of the box exposed.

Boxes produced in this way in large quantities are finished by means of a "banding" machine in which a reel of glazed paper is gummed on one side and drawn on to the box which is automatically turned four times by the machine and thus covered.

Wire-stitched Boxes.—The board used for this class of box is cut into required sizes and either scored or dented. In the latter case the board is passed through a denting machine which stamps a slight depression along the line which is to form the corner of the box.

The ends of the board are then slotted so that the box can be produced by being turned up into shape along the lines formed by the denting machine. The ends are then fastened together by the *wire stitching*, in which process small pieces of wire are forced through the ends of the box and clinched.

Metal-edged Boxes are generally manufactured from good material, such as leather boards, because they are intended for constant use. The boards are usually grooved along the bending line, either with a square groove or with a deep V-shaped groove, the latter being preferred as giving the box a neater finish at the corners when completed. The edges of the box and the joints are finished off with metal edging which consists of a thin strip of metal stamped out and provided with sharp projecting points. When this strip is forced into position the projections pass through the board and being turned up by the machine are firmly clinched. The boxes made by this process are very strong and present an attractive appearance.

Folding Cases.—The cheap common cases used for packing eggs, patent medicines, and similar articles of domestic use are stamped out from thin cardboard by machinery. The general shape and outline of the boxes having been calculated, a metal forme or template is prepared, by means of which the outline of the box can be stamped out.

The forme resembles in principle that used by a printer, but instead of raised type, strips of brass are used and also pieces of hardened steel. When the thin board is placed on the forme and submitted to pressure, the brass strips indent the board along the lines which are to form the edges of the box, and the steel knives cut out the portions of the board which are not required. The two edges which overlap to form one side of the box are fastened together with wire stitching or with glue. In this condition the box can be folded flat, and when required for use it can be opened up and put together as a box very quickly.

Postal Tubes, etc.—The many varieties of cylindrical boxes made for postal work, the packing of gas mantles, phonograph records, carbon paper, blue print and photographic papers, and similar purposes, are made by covering one side of a board with glue or some adhesive material, and rolling the board up into the form of a tube on an iron roller, the diameter of which varies according to the size of the bore of the tube.

For short boxes the long tubes are cut up into stated lengths. The caps for these tubes are stamped or pressed out of circular discs of flexible leather board. The whole operation is exceedingly simple and does not require any elaborate explanation.

CHAPTER VIII

THE UTILISATION OF WOOD WASTE

Various methods of utilising wood refuse are in practice, chiefly based on chemical processes. The only commercial application of waste wood based on a simple mechanical treatment, and now an extensive industry, is the manufacture of wood wool.

Wood Wool.—This is an elastic material much used for stuffing cushions and mattresses; for packing glass, hardware, and fragile goods; for filtration, and many other purposes of diverse character. It is very light and bulky, not easily reduced in volume when wetted, and is thus eminently suited to these and similar uses.

Any small odds and ends of wood from carpentering and cabinet workshops up to 14 or 16 inches long can be utilised.

Special machinery has been devised for converting pieces of wood of all shapes and sizes into shavings of desired thickness. The pieces of wood are fed to the machine by hand. They are seized by rollers which carry the wood forward automatically, bringing them under planing irons and also in contact with pointed knives, the thickness of the shaving being determined by the setting of the plane irons and the width of the shaving being fixed by the position of the knives which produce cuts in the wood parallel to the lengh. One machine is capable of producing 6 to 12 cwt. of wood wool in twelve hours.

Sawdust.—Large quantities of sawdust are produced in many industries, and the profitable utilisation of this waste material depends largely upon the quantity periodically available. When the amount is small, it is best utilised as an ordinary packing material, but for this there can only be a limited demand. Some idea of the varied uses of sawdust may be gathered from the following brief description of the methods in use.

Sawdust thoroughly mixed with common rosin is converted into fire-lighters.

Mixed with highly concentrated artificial manures, it serves as a medium for manurial purposes. The sawdust itself has no value as a fertiliser, but it has a capacity of absorbing and retaining liquids. Occasionally the sawdust is first converted into charcoal.

Sawdust has also been employed as the source of the carbon in calcium carbide. The sawdust is first converted into charcoal, which is mixed with limestone, and the mixture heated for several hours in an electric furnace.

In limited quantities, sawdust is also converted into paper pulp, but the fibre is exceedingly short and of little value, and it is difficult to obtain an evenly boiled material owing to the difficulty of maintaining a proper circulation of the caustic soda, lye, or other reagent in the digestor.

Sawdust is also mixed with the concentrated waste liquors from the sulphite wood-pulp manufactories, and then converted into briquettes. These briquettes can be used as fuel or submitted to distillation for the manufacture of wood spirit, acetic acid, and charcoal.

Producer Gas from Wood.—An interesting application of the use of waste wood is to be found in the generation of "power gas." In Riché's gas-producer the wood is heated in two suitable retorts, one of which is used for the distillation of the wood, and the second for the decomposition of the gases obtained by the distillation of the wood in the first retort. The combustion is first started in the second or reducing retort. When the heat has been raised to the proper extent, the distillation is commenced in the first retort. The charcoal produced is withdrawn periodically from the bottom of the first retort and thrown into the reducing retort. The distilled gases from the first retort are passed through the heated charcoal placed in the second, and subsequently into the gas holder. The gas produced has a heating value of about 340 B.T.U. per cubic foot, the quantity of gas per 100 kilos. of wood being 100 cubic metres, or about 16 cubic feet of gas per pound of wood.

Donkin[1] states that about 100 small plants of this type have been erected in France and some of the French colonies. An interesting example is to be found in Madagascar, where gas obtained in this way is utilised in two gas engines of 15 and 8 h.p. respectively for the manufacture of artificial ice, the cost of the motive power being one-third of that obtained by usual methods.

Oxalic Acid.—Sawdust and other forms of wood waste yield oxalic acid when treated with caustic soda. Forty parts of sawdust are mixed with strong caustic soda of specific gravity 1·35, and heated in shallow pans until the temperature rises to 220—240° C. The product contains

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[1] "Gas and Oil Engines." B. Donkin.

carbonate of soda and sodium oxalate. This is dissolved completely in boiling water, and the strength of the solution carefully regulated, so that on cooling, the sodium oxalate crystallises out. The mixture is then treated in the hydro extractor to remove the liquid.

The crystals of sodium oxalate are dissolved and treated with milk of lime, and thereby converted into calcium oxalate. The latter product is precipitated, separated from the liquor by filtration or any suitable means, and repeatedly washed with water.

The calcium oxalate is then decomposed by treatment in a lead-lined vessel, with strong sulphuric acid, the whole mixture being heated with steam, and maintained at the boiling point for some time. The oxalate is decomposed, giving, after treatment with the sulphuric acid, a precipitate of calcium sulphate and a solution of oxalic acid. The precipitated calcium sulphate is removed, and the solution carefully evaporated for the production of crystallised oxalic acid.

The amount of oxalic acid obtained may be varied according to the method of heating. Thus the percentage yield is increased by using potassium hydrate as well as sodium hydrate, and also by heating the material in thin layers. The yield of oxalic acid from various woods is as follows:—

Spruce	94·7
Poplar	93·0
Beech	86·3
Oak	84·4

THE DESTRUCTIVE DISTILLATION OF WOOD.

When wood is burnt under conditions which restrict the supply of air, or heated in closed retorts, it passes through a process of *destructive distillation* with the production of certain valuable commercial substances.

The combustion of wood in a confined space was resorted to in early days for the manufacture of charcoal simply, and large quantities of this charcoal are produced even to-day by the primitive method of stacking wood, covering it with earth and setting fire to the wood at the bottom of the pile. The only substance obtained was the charcoal left when the process was completed, but about 1812 the discovery of the presence of wood spirit and acetic acid in the vapours given off, led to a closer study of the chemical changes taking place.

The products of distillation are chiefly acetic acid, wood spirit (methyl alcohol) tar, gases and charcoal. By slow distillation at a low temperature a maximum yield of acetic acid and tar is obtained. The gas given off during the operation, a mixture of carbon dioxide and carbon monoxide, is utilised by passing it through the furnace employed in heating the retorts. The carbon dioxide is reduced to monoxide, a combustible gas which gives off its available heat in the furnace.

By rapid distillation at a high temperature, the volatile products are decomposed giving a greater yield of gas and a smaller proportion of acetic acid.

The effect of the method of heating is shown in the following table taken from Fischer's Chemical Technology. In the *slow* distillation process, the wood was heated slowly for six hours, starting with cord retorts, while in the *fast* distillation the wood was placed at once in heated retorts and treated for three hours.

Percentage yield of distillation products.						
Wood.	Total distillate.	Tar.	Wood vinegar crude.	% pure acetic acid.	Dry charcoal.	Gases.
Birch—						
slow . .	51·05	5·46	45·59	5·63	29·64	19·71
fast . .	42·98	3·24	39·74	4·43	21·46	35·56
Beech—						
slow . .	51·65	5·85	45·80	5·21	26·69	21·66
fast . .	44·35	4·90	39·45	3·86	21·90	33·75
Oak—						
slow . .	48·15	3·70	44·45	4·08	34·68	17·17
fast . .	45·24	3·20	42·04	3·44	27·73	27·03
Larch—						
slow . .	51·61	9·30	42·31	2·69	26·74	21·65
fast . .	43·77	5·58	38·19	2·06	24·06	32·17
Spruce—						
slow . .	46·92	5·93	40·99	2·30	34·30	18·78
fast . .	46·35	6·20	40·15	1·78	24·24	29·41

In practice the distillation of wood is carried out with due regard to the nature and quantity of the desired products, and the method of treatment varied accordingly.

Steam Distillation.—With pine and woods rich in turpentine oils the material previously reduced to the condition of small chips is heated by means of steam in closed vessels at a pressure of 40 lbs., and the oils distilled off by the steam.

This process is usefully employed in the pulp mill, since the manufacture of paper pulp from pine wood can be conducted in such a way as to ensure the extraction of the turpentine from the digestors and the subsequent conversion of the wood into pulp. The soda process of paper-making is easily adapted, for the ordinary steam pressure is sufficient to drive off all the volatile oils, and most of the resinous matters are converted into soluble soda compounds.

Dry Destructive Distillation.—The products obtained from different woods as determined by the Bureau of Chemistry, Washington, are shown in the following table :—

Average yield per cord of wood (128 cubic feet piled wood).			
	Hard woods.	Resinous woods.	Hard wood sawdust.
Charcoal (bushels)	45	30	30
Crude wood spirit containing acetone (gallons)	10	3	3
Acetate of lime (lbs.)	75	120	60
Tar (gallons)	15	45	—
Wood oil (gallons)	—	45	—
Turpentine (gallons)	—	10	—

In the slow distillation process, a maximum yield of solid product is aimed at, with a minimum quantity of gas. Harper gives the results of a test on dry yellow pine :—

Yield per cord, air-dry.			
	Gallons.	lbs.	%
Turpentine	18·64	134·20	3·679
Wood oil	11·09	86·50	2·371
Tar	96·0	846·72	23·216
Acid	96·0	830·49	22·771
Cake	—	14·74	·404
Charcoal	—	796·00	21·826
Yellow oil and pitch	6·78	57·02	1·563
Gas and Loss	—	881·33	24·170
		3,647·0	100·000

With the rapid distillation method, a maximum yield of gas is obtained, and in this case the process is utilised for the manufacture of illuminating gas or for power gas. All kinds of waste wood material such as sawdust are turned to good account in this way.

CHAPTER IX

TESTING OF WOOD PULP FOR MOISTURE

In the selling and buying of wood pulps the question of associated moisture is of obvious importance, regulated by convention and by standards, it requires to be controlled by actual tests. The mechanical wood pulps are generally shipped from the mills in the form of bales containing moist pulp on the basis of 50 per cent. air-dry pulp. The chemical pulps are shipped usually in bales containing the air-dry pulp.

Disputes frequently arise as to the exact air-dry weight of pulp received, the chemical pulps frequently containing moisture in excess of the standard, and the mechanical pulp also containing a larger amount of moisture than 50 per cent.

No satisfactory standard method has yet been found for the sampling and testing of wood pulp. When the freshly made bales are shipped from the pulp mill so that the whole of the sheets in the bale are uniform, then it is comparatively easy to take samples from the bale which shall fairly represent the pulp. If, however, the distribution of moisture in the bale has been altered to any extent, either by loss in weight owing to the drying of the outer sheets and exposed edges of the bale during prolonged storage, or on the other hand if the bales have become much heavier by accidental wetting through rain or other causes, then the sampling is by no means an easy matter.

Frequently the water in the bale freezes, and in consequence of this much of the water is drawn from the interior of the sheets and deposits itself as a layer of snow or ice between the sheets which lie upon one another in the bale.

The bale when opened falls apart most readily just at those points where the surface of the sheet is covered with ice, and it is almost impossible under such circumstances to take out samples that shall fairly represent the whole bale. Even when this ice has thawed out sufficiently to resume the form of water, it does not distribute itself evenly through the pulp for a very long period.

General Principles.—A certain proportion of the bales which form a consignment are selected for the test. Usually 4 per cent. of the number of bales are taken, due care being exercised in the selection so that the bales are sound, in good condition, and do not exhibit any serious deviations in gross weight.

The selected bales are weighed and sampled. The samples as cut are immediately put into bottles, or tins, which are sealed up and taken to the laboratory where they are dried at a temperature of 100° C. and the percentage of absolutely dry pulp determined. The weight of air-dry pulp is calculated from this figure on the arbitrary basis that 90 parts of absolute dry pulp give 100 parts of air-dry pulp.

The analyst gives a certificate in accordance with the following schedule:—

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

Pulp, said to consist of bales, marked

lying at

The samples were drawn by me on

	Bales.	T.	Cwt.	Qrs.	Lbs.
Total gross weight of bales sampled (intact) .					
(*For numbers and detailed weights see below.*)					
Weight of Parcels calculated from above . .					
Percentage of absolutely dry pulp in the sample				per cent.	
,, moisture in the sample . .				,,	
,, air-dry or moist pulp in the parcel on the basis of 90=100 (air-dry) .				,,	
45=100 (moist) .				,,	
,, excess Moisture, Fibre . .				,,	

	T.	Cwt.	Qrs.	Lbs.
Weight of Pulp to be invoiced				

NUMBERS AND DETAILED WEIGHTS OF BALES SAMPLED.

Analyst.

Difficulties in Sampling.—In practice it is found that the testing of wood pulp for moisture offers many difficulties. The uniformity of the moisture throughout the bale is seriously disturbed by the causes already described so that not only is it difficult to select really representative bales, but the work of cutting out samples is also complicated.

Various methods are employed for taking out samples of pulp, and at present there is no standard method, although attempts have been made to establish a uniform system.

It is scarcely necessary to enter into any prolonged discussion as to the merits of the various methods each of which are no doubt correct under certain conditions. With pulp that has not been in stock more than three or four weeks any reasonable system would give correct results, but the difficulty is to find a system which would give correct results on freshly made pulp and exactly the same results on the pulp after having been in stock several months.

Probably the system which finds general favour is that known as the "wedge" method, in which it is assumed that a wedge having its apex at the centre of the sheet of pulp and a base of any desired width at the outer edge of the sheet of pulp represents the sheet itself, taking the correct proportions of the inner and outer sections of the sheet. This may be explained by reference to the diagram in Fig. 23.

Let ABCD represent a sheet of air-dry pulp of uniform thickness, measuring 24 inches by 18 inches, and divided into four equal parts—E, the inside portion; H, the outer portion; and F, G, intermediate portions, thus:—

		Square inches.
Area E	= 12″ × 9″	= 108·0
Areas E, F	= 16·975″ × 12·73″	= 216·0
Areas E, F, G	= 20·785″ × 15·585″	= 324·0
Areas E, F, G, H	= 24″ × 18″	= 432·0

Square inches.
E = 108
F = 108
G = 108
H = 108

Total = 432

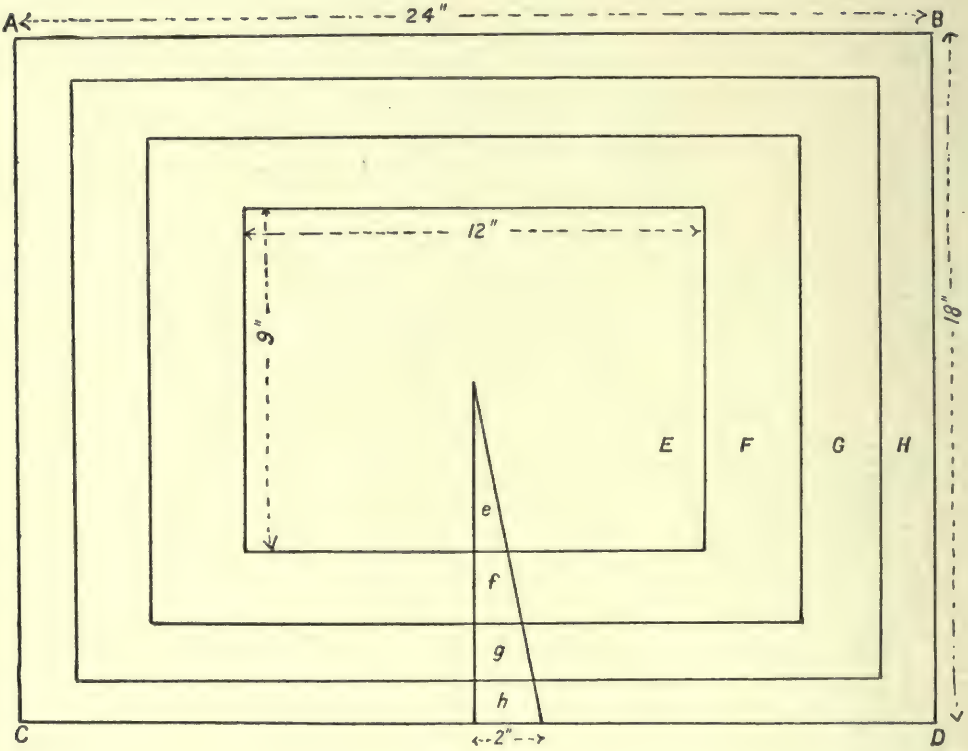

FIG. 23.

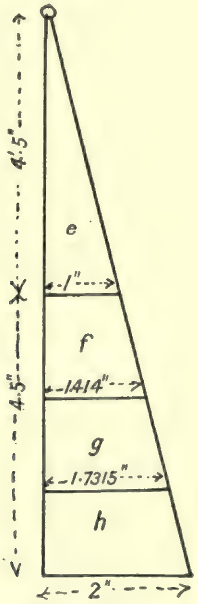

FIG. 23A.

The dimensions of the various rectangles are all proportional, that is, the ratio of the length to the breadth is the same in all cases, viz., 24 to 18.

A sample from the sheet which shall represent the whole is obtained by taking equal areas from each of the pieces E, F, G, H; but in practical testing such a course is impossible, as it would necessitate marking the exact position of the "lines of separation" before the small pieces of equal area could be cut. Another alternative would be to cut a quarter sheet from the whole—an equally impracticable scheme. But a wedge gives four equal-sized pieces from the four areas E, F, G, H.

Let such a wedge having a base of, say, 2 inches, be drawn as shown in Fig. 23. Let Fig. 23A represent the wedge on an enlarged scale, consisting of the four areas *e*, *f*, *g*, *h*. The area of the whole sheet is 24 inches by 18 inches, or 432 square inches, and the areas of the wedge is that of a triangle whose height is 9 inches and whose base is 2 inches.

The wedge contains a series of triangles, viz., (1) the triangle *e*; (2) triangle consisting of pieces *e f*; (3) triangle consisting of *e*, *f*, *g*; (4) triangle consisting of pieces *e f g h*. By calculating the area of each triangle the exact size of the separate pieces *e*, *f*, *g*, *h* is found.

The height and base of each triangle is easily calculated:—

(1)
$$\frac{\text{Base of triangle } e}{\text{Base of triangle } (efgh)} = \frac{\text{Height of triangle } ef}{\text{Height of triangle } (efgh)}$$

$$\frac{\text{Base of } e}{2} = \frac{45}{9} \text{ giving } 1{\cdot}0 \text{ inches.}$$

$$(2)\quad \frac{\text{Base of triangle } ef}{\text{Base of triangle } (efgh)} = \frac{\text{Height of triangle } ef}{\text{Height of triangle } (efgh)}$$

$$\frac{\text{Base of } ef}{2} = \frac{6{\cdot}365}{9} \text{ giving } 1{\cdot}4144 \text{ inches.}$$

The other triangles are treated in a similar manner and the areas readily calculated.

(Area of a triangle $= \frac{1}{2}$ base × height.)

			Square Inches.
Triangle *hgfe*	has area	$\frac{1}{2}(2 \times 9)$	$= 9$
,, *gfe*	,,	$\frac{1}{2}(1{\cdot}7315 \times 7{\cdot}7925$	$= 6{\cdot}75$
,, *fe*	,,	$\frac{1}{2}(1{\cdot}4144 \times 6{\cdot}365)$	$= 4{\cdot}50$
,, *c*	,,	$\frac{1}{2}(1 \times 4{\cdot}5)$	$= 2{\cdot}25$

From the above figures the areas of the pieces *e*, *f*, *g*, *h*, are:—

Square Inches.
$e = 2{\cdot}25$
$f = 2{\cdot}25$
$g = 2{\cdot}25$
$h = 2{\cdot}25$

Hence any sized wedge contains what the pulp maker defines as correct proportions of "inside and outside pulp," at any rate mathematically.

Absolute Dry and Air-dry Pulp.—The exact air-dry weight of pulp is calculated on the basis that 100 parts of air-dry pulp consists of 90 parts absolute dry pulp and 10 parts of natural moisture. This is an arbitrary figure based on the assumption that air-dry pulp contains 10 per cent. of natural moisture. As a matter of fact the air-dry weight of pulp varies according to the conditions of the atmosphere, but for trade purposes the arbitrary figure selected is convenient.

In 1896 Sindall made some experiments with a view of determining the influence of the atmospheric moisture upon the weight of wood pulp. Numerous samples were exposed to ordinary atmospheric conditions for nearly two years, the samples of pulp being weighed two or three times a week and the relative humidity of the air being also noted. The following table was compiled as the result of these experiments, showing the air-dry weight of the exposed pulps, the actual absolute dry weight of pulp being 88 parts in each case.

SHOWING THE VARIATION OF THE WEIGHT OF PULP DUE TO MOISTURE IN THE AIR.

Relative Humidity. H.	Mechanical Pulp.	Sulphate and Soda Pulp.	Sulphite Pulp.
	Average.	Average.	Average.
51·4	99·03	95·98	96·53
60·00	100·04	96·42	96·85
65·30	100·42	96·91	97·45
77·20	102·24	98·60	99·30
80·13	102·41	98·21	99·30
82·10	102·78	98·41	99·74
82·70	102·58	98·70	99·69
82·90	102·84	98·78	99·80
83·20	103·55	98·95	100·50
83·90	103·17	98·98	100·63
85·10	103·81	99·42	100·60
86·60	105·13	100·41	101·63
87·50	104·55	99·92	101·04
88·24	104·64	100·23	100·93
89·10	104·63	100·02	101·14
90·00	105·40	100·70	101·90
93·00	106·82	102·40	103·76

The exact relation between the humidity of the air and the air-dry weight of wood pulp as determined by these experiments may be expressed in the following way:—

If the numbers representing humidity form a series in arithmetical progression, then the weight of wood pulp corresponding to those numbers produces a series of figures in geometrical progression, thus:—

$$\text{Humidity} = H,\ H + d,\ H + 2d,\ H + 3d,\ H + 4d,$$
$$\text{Weight} = W,\ Wr,\ Wr^2,\ Wr^3,\ Wr^4,$$

Where $d = 5$, $r = 1{\cdot}28$.

If the results given in the table are plotted in the form of a curve, it is possible to correct the errors of observation and determine the air-dry weight of pulp for every 5 degrees difference in the humidity of the air.

SHOWING THE VARIATION OF THE WEIGHT OF PULP FOR EACH 5 DEGREES INCREASE IN THE HUMIDITY OF THE AIR.

Relative Humidity. H.	Air-dry Weight of Pulp.			Average difference for 5° H.	Constant r.
	Mechanical.	Sulphate and Soda.	Sulphite.		
50	98·95	95·90	96·35	0·26	—
55	99·30	96·10	96·60	0·33	1·25
60	99·70	96·35	96·95	0·42	1·27
65	100·20	96·65	97·40	0·52	1·24
70	100·80	97·05	97·95	0·68	1·30
75	101·60	97·60	98·65	0·82	1·30
80	102·50	98·30	99·50	1·13	1·35
85	103·75	99·35	100·60	1·52	1·34
90	105·25	100·80	102·20	—	—
					Mean=1·28

CHAPTER X

WOOD PULP AND THE TEXTILE INDUSTRIES

The celluloses and compound celluloses are produced in definite and characteristic structural forms, and only in such form. By chemical processes such as described in Chapter II., we may convert the original structural celluloses into its amorphous or structureless forms by way of solutions of derivative compounds. It is clear, however, that questions of form and dimensions underlie every technical problem involved in the applications of cellulose.

The following are the dimensions of the more important celluloses, considered as ultimate fibres.

		Length of Fibre.		Diameter.
Fine textiles.	Cotton	20—40	mm.	—
	Flax	25—30	,,	0·015—0·037
	Rhea	60—200	,,	0·030—0·070
	Hemp	15—25	,,	0·016—0·050
Coarse textiles and Rope-making.	Jute	1·5—4·0	,,	0·020—0·025
	Sisal	1·5—6·0	,,	0·015—0·026
	Phormium	5·0—15·0	,,	0·010—0·020
	Pinewood (Tracheids)	1·0—20·0	,,	0·015—0·020
Paper-making	Esparto	0·5—3·0	,,	0·010—0·018

It is somewhat remarkable that the most important cellulose, cotton, occurs and is industrially worked as an ultimate fibre or structural unit.

Incidentally, it is worthy of mention that cotton is a seed hair, and in physiological function therefore, being concerned with a usually perishable tissue, it is not *a priori* associated with permanence. On the same grounds and for the contrary reason we should expect to find in the wood substances which have long continuing or perennial functions, a chemical constitution implying superior stability. The paradox, however, holds that cotton is our type of chemically balanced cellulose and of a higher order of stability than the wood celluloses.

To complete this point we must refer the reader to the previous section, which deals with the conditions of permanence of the ligno-celluloses which are natural compound forms. We have to remember also that a wood *cellulose* is a residue always of chemical processes.

As regards structure the woods are highly complex, whereas most of the textile fibres mentioned above are either bast fibres (bundles) or fibre vascular bundles. In the former case, as in flax, rhea, and hemp, the bundle is simple. It is more complex in the case of jute (see Chap. I.), and still more complex in the fibre vascular bundles of monocotyledons.

Esparto is a heterogeneous aggregate as in the case of the woods.

In the more complex structures the celluloses are associated with various chemical groups (compound celluloses), which are attacked and removed by the various treatments of hydrolysis and oxidation by which the celluloses are isolated. For our present purpose we are concerned only with the celluloses in the form of ultimate fibres. These are the unit elements of structure of the yarns and threads which are the basis of textile fabrics. The mechanical properties of these, as well as the processes by which they are mechanically prepared and ultimately spun, are obviously determined by their simpler elements of form—that is, their dimensions.

The mechanical principles involved in the production of fine textile yarns from these discontinuous units, are first, the reduction of these to a common untwisted sliver, in which they are parallelised; secondly, the drawing and twisting of the fibres composing the sliver in continuous length.

The tensile properties of the resulting yarn depend mainly upon the twist, partly upon the adhesion of the more or less closely-spun fibres.

There are numerous variations of the process, such as the wet spinning applied to bast fibres and notably flax, the passage of the sliver through a bath of warm water facilitating the ultimate subdivision of the bundles of fibres in the final drawing and twisting operation. In the coarser textiles, such as jute, it is evident that the spinning unit is an aggregate or bundle of the ultimate fibres, which are too short (2 to 3 mm.) to admit of manipulation.

They are worked in lengths, which have reference to the conditions of the machinery, most convenient for preparing, drawing, and twisting. But it must be borne in mind as a fundamental technical fact that the ultimate properties of the yarn are conditioned primarily by the length of the ultimate fibre. This will be evident from the table (p. 232), giving the relative strengths of textile yarns in terms of actual tenacity and apparent elasticity (extensibility). We have added to the list the new products known as artificial silk, or lustracellulose. This being prepared from structureless solutions of cellulose derivatives may be considered as structureless. In this sense they resemble the true silks which are produced in solution in the glands of the silkworm and extruded into the atmosphere, the worm performing the mechanical operation of drawing and laying the threads in the specialised form of cocoon.

The structureless cellulose, in the form of a thread of regular dimension, presents to us a case of mechanical properties of a substance independently of the grosser structural details which characterise the natural cellulose fibres, and it will be seen that cellulose admits of very severe treatment in passing through a cycle of operations and reverting to an amorphous substance which retains much of the structural properties of the original.

Reverting now to the fibrous celluloses, there are certain features common to the paper-making and the textile industries. Thus, a web of paper and a textile yarn may be made from the same raw material, and, moreover, have the common characteristic of an agglomerate of discontinuous fibrous elements produced in continuous length. The strength or cohesion of the two fabrics depends in the first place upon the surface adhesion of the fibrous units, but in the case of the textile yarn this is a much less important factor than the "twist" communicated by the spinning process. On the other hand the paper web, though devoid of twist, presents certain characteristics in the opposition and adhesion of its structural units, which makes it a more coherent agglomerate than the yarn. Generally this is referable to the wet processes of the paper-maker, which brings the colloidal fibre substance into a condition of hydration or gelatinisation, in which a more intimate adhesive contact of the fibre surfaces is determined. The cohesion is augmented by the pressure to which the web is subjected while still in the wet state and the union of the fibre surfaces is finally cemented by the drying or dehydration of the web. Conversely, when re-wetted a paper is brought back into approximately the condition of the web as first put together and its cohesion in this state or wet-strength, is only a fraction of that of the paper. The cohesion of a textile yarn, on the other hand, is only slightly affected by wetting, and the effect indeed is not necessarily in the direction of diminishing tensile strength.

The main point of contrast between these great divisions of manufactures devoted to the industrial utilisation of the vegetable fibres, is the length of the unit fibre, or fraction of fibre, in the final state of preparation of the raw fibrous material. Generally, we may say that the limit of economic handling in the textile industry is reached with a length of fibre of 3—5 mm. This inferior limit expresses, on the other hand, the outside limit imposed upon the paper-maker for the satisfactory working of his wet web upon the wire cloth of the machine or hand mould, and for the majority of papers a length of 1—2 mm. is a working optimum.

This corresponds with an obvious complementary relationship of the two industries, and the paper-maker, up to fifty years ago, was practically limited, as to raw material, to the wastes of the textile industries.

In later times there have been notable advances in the method of working up short fibre wastes by the spinner's dry methods, "ginning process," and, by special modifications of teasing or carding machines, the utilisation of these short fibres has been carried to extreme limits. As a question of cost of production it is found, however, that the paper-making process has considerable advantage. The problem then arises of converting the continuous length of paper into a textile yarn, with the associated question of the actual utility of the product. The elements of the problem are these:—

(1) The subdivision of the web of paper into strips of suitable dimensions.

(2) The rolling of these strips continuously into the cylindrical form.

(3) Subjecting the cylindrical length of paper "felt" to a twisting operation so as to increase its tensile strength to a maximum.

Having by these processes appreciated to a maximum the tensile qualities of the fibrous agglomerate, we still have to reckon with the intrinsic limitations of quality, due to shortness of fibre, on the one hand, and the fact that when wetted the product loses its cohesion.

This is a general and somewhat "theoretical" *exposé* of the technical basis of an industrial movement which has been in progress since 1891, toward the utilisation of paper in the form of a textile. It may be noted that this movement, though quite new to Europe, is based upon old-world practice, for the Japanese have for centuries used paper as a basis of string or twine, twisting paper strips of convenient width into the cylindrical form, and also piecing successive lengths to produce a virtually continuous fabric. This, however, was a manual operation performed upon the finished paper, and the product is only crudely suggestive of the pulp yarns which have been evolved through various stages of perfection by the work of European inventors bringing to bear upon the problem the resources of modern mechanical appliances.

The development of this industry is mainly due to the enterprise of a succession of German inventors, and an excellent account of their labours is contained in the treatise of Prof. E. Pfuhl, "Papierstoffgarne (Zellstoffgarne, Xylolin, Silvalin, Miella) ihre Herstellung, Eigenschaften und Verwendbarkeit," published by G. Höffler, Riga, 1904. This treatise on "Paper-pulp-yarns, their preparation, properties and applications," is a very complete technological account of the matter, to which the specialist student must refer. In the general account which follows we have made free use of the matter of the treatise, and we acknowledge our indebtedness to the author and publisher.

It appears that the evolution of the industry is set forth in the subjoined outline of inventions, as embodied in German patents. Practical success is claimed to have been achieved by three of these systems, each of which represents a consolidation of two or more patented inventions :—

(a) The system of Claviez & Co. is based upon a finished but unsized paper as raw material. This is cut into fine strips, of a few mm.'s width, each strip being separately wound on a bobbin, which is then transferred to a spinning or twisting frame. In the form of twist it is subject to a rolling process to consolidate the thread, and this treatment is repeated, after moistening the thread, in a second machine, the speed of which is adjusted to produce a certain drawing effect.

The spindle designed by Claviez for the spinning or twisting of the paper strips is represented by the accompanying figure (Fig. 24), the spool or reel carrying the paper strip of 2—3 mm. width is carried on the hollow brass axis *b*, which is held in position on the spindle *s* by means of springs. The fliers *f* rotate in the same direction in which the paper strip was wound on the spool; the strip is thus twisted and drawn off through rollers under suitable tension. The yarns produced under this system are known as "Xylolin," and they are stated to have firmly established themselves in the textile industry, competing chiefly with jute yarns.

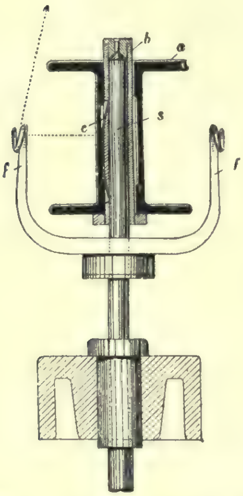

FIG. 24.—Spindle for twisting paper-strips.

a carries the continuous length of paper of 2—3 mm. width: *f f* are the fliers.

(Claviez & Co., D. R. P. 93324.)

A considerable refinement in production has been aimed at in the two groups of inventions about to be described, for which the starting point is not a finished paper, but the web in the unfinished condition in which it is delivered from the press rolls of the paper machine.

(b) The Kellner-Türk system is the consolidated result of the inventive work of the late Carl Kellner, of Hallein—a well-known pioneer of the wood pulp industry—and of G. Türk, of Bad Gastein. The main patents are those of 1891 (D. R. P. 73601) and 1892 (D. R. P. 79272) and the claims are similar, the former indicating the formation of a pulp-sliver by taking moist paper strips as delivered from a cylinder paper machine, and subjecting them whilst still on the cylinder wire to a rubbing and rolling treatment by which they are rounded and consolidated; the latter patent indicates the same general plan of manufacture, but the rolling of the strips takes place after they have left the machine wire. The production of the paper or pulp strips is not patented. This is effected by the special construction of the wire cloth of the paper-making cylinder, which is an alteration of impervious brass strips with the ordinary 60 — 70-inch mesh wire cloth; the pulp is deposited on the latter only. These patents were acquired in 1900 by the Patentspinnerei A.G., in Altdamm, Stettin, in whose hands the process was further developed in the direction of the Türk patent.

The main feature of the treatment of the strips is the process of conversion from the flat to the cylindrical form, under which there is an incidental consolidation of the fibrous aggregate. This effect is produced by passing the strips through a special apparatus, the principle of which may be traced to an invention of O. Schimmel & Co., Chemnitz, described in the German patent 76126, above cited. The invention was in its inception applied to the "lap" of dry-carded short fibre as delivered from a textile carding machine. The lap delivered at the full breadth of the card is received between a pair of rollers which divide it by a peripheral cutting arrangement into narrow strips, which pass forward to the rolling apparatus. This consists of an upper and under endless band of leather in close contact, disposed for motion in the horizontal plane, each round a pair of rollers moving in geared connection. The rotation of these rollers carries forward the now divided strips, but an alternating movement in the direction at right angles is communicated to the leather bands by eccentrics, and this movement is in turn communicated to the strips as they travel forward, under which they are continuously rubbed and rolled into cylindrical form. They are then suitably laid down in receivers, to be transported to the spinning or twisting frames (see Fig. 25).

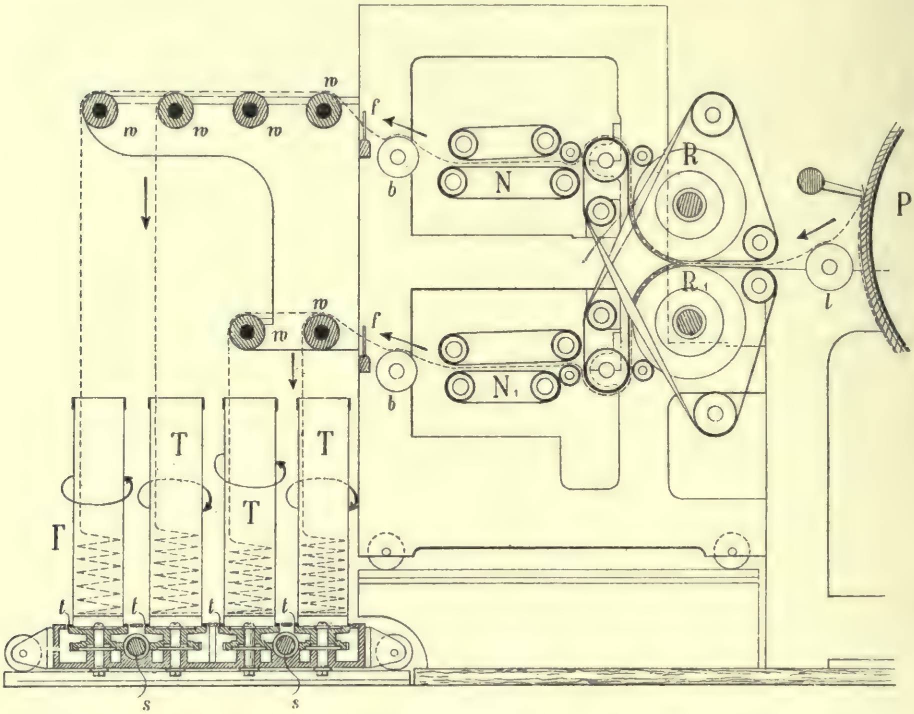

FIG. 25.—Machine for rolling flat strips of prepared short fibre (sliver). The "lap" is taken from the card P, sub-divided into strips in passing R R, rolled at N N, and delivered into cylindrical boxes or cans, T T. (O. Schimmel, D. R. P. 76126.)

On the Kellner-Türk system, as applied to the wet pulp strips, a similar apparatus and process succeeds the press-rolls of the paper machine. The endless bands of the rubbing and condensing rollers are in this case made of indiarubber.

The third operation, that of spinning or twisting, is carried out on the still moist thread. There are various devices employed in the textile industry for conferring the high degree of twist which characterises the textile yarns in their final forms; the same principles and forms of machine are pressed into the service of the paper-pulp-spinner. The twisting is mostly carried out on "Ringzwirnmaschinen," ring-spindle machines, *i.e.*, frames carrying 60—70 spindles on the side. In making weft yarns, the delivery of the spun yarn is varied so that it may be wound directly into cops, or on to tubes placed over the spindles. There are two limitations to the efficiency of this system; one is in the mode of making the pulp strips on a *cylinder* machine. The alternative process and machine, based on the flat-running Fourdrinier wire, with its much higher productive efficiency, is adopted by them as the basis of the competing system which we shall next describe. The contrast of these two methods of converting beaten pulp into paper is well set forth in C. Hofman's *Handbuch der Papierfabrikation*, ed. 1897, page 858.

The second limitation of efficiency—that is, in output and therefore economic production—is in the speed of the machine and process of rounding and consolidating the strips. Taking 12—15 m. per minute as the speed of running, a machine of 80 spindles will produce in length from $12 \times 80 \times 60 \times 24 = 1{,}382{,}400$ m. to $15 \times 80 \times 60 \times 24 = 1{,}728{,}000$ m. per diem: these lengths represent 460 to 576 kilos. of a No. 3 yarn, or 115 to 144 kg. of a No. 12 yarn. In actual working, allowance has to be made for unavoidable breaks and stoppages, and the output is taken at 30 per cent. less than these figures. It may be noted that a beating engine (Hollander) of 160 to 200 kg. capacity (dry pulp), dealing with four charges in the twenty-four hours, would feed two of such special machines.

In summing up his notice of this system, Prof. Pfuhl expresses himself as follows (page 33):—"It is probable that a number of circumstances, in addition to the not very satisfactory output of the sliver machine, have contributed to the present position (end of 1906) of the system, which is that after many years of existence, as indicated by the dates of the patents, it remains without industrial extension."

In connection with the development of the Kellner-Türk process, a number of patents have been taken by Leinweber, which have been acquired by the Altdamm Company. These inventions have reference to details which are found to be essential factors of economic production, such as the subdivision of the web of pulp into small strips (D.R.P. 140011). The mode of distributing these to the further operations (140,666) a further patent (140012) has reference to the rounding of the strips to a sliver by causing them to pass through a funnel, the tube of which is of spiral or other special construction, this treatment immediately preceding the spinning or twisting.

System of R. Kron. "Silvalin" yarns.

It will have been evident during this discussion that wood-pulp "spinning" is a hybrid process: a cross adaptation of well-known paper making and textile methods to the production of a particular type of fabric, and involving in a very special sense the question of cost of production. It may be noted in illustration of this point that while papers and staple textiles are produced and sold under a very wide range of costs and prices, the new industry in the hybrid products depends mainly upon cost of production. The system which consolidates the inventions of Messrs. Kron claims important progress in this essential element of success. In the first place, the production of the original pulp-strips is "intensified" by employing the ordinary Fourdrinier machine at its full width, the web being subdivided into narrow strips by an arrangement for projecting jets of water upon the web at such distances that the web is divided into 100—500 strips per metre. The separation of the strips is, however, not thus completed; they are wound up on a roll of the full width, and are afterwards separated and detached as discs. It is based upon the following patents, of which the subject-matter indicates the essence of the several inventions :—

I. Main patent (K. 23200 vii/76c). A process for twisting or spinning the cellulose (pulp) directly from pulp-rolls.

(a) Addition-patent I. (K. 23887 vii/76c) for winding up the wet-web at the breadth of the machine to be afterwards divided in pulp-discs of suitable narrow width.

(b) Addition-patent II. (K. 23926, vii/76c). Improvements in the manufacture of pulp-rolls in a moist but coherent state.

II. Main patent (K. 25168, vii/76c). Process and apparatus for winding up moist strips of paper pulp, etc.

III. Main patent (K. 25043). Process and apparatus for sub-dividing a web of pulp (as on the wet end of a paper machine) into strips.

IV. Main patent (K. 26001). Apparatus for direct delivery of moist pulp strips.

V. Main patent (K. 25036). Spinning machine for preparation of detachable cops.

The succession of operations in the Kron system is as follows:—

1. The formation of the web on the Fourdrinier wire; its sub-division into strips by the impact of jets of water for the number of strips required to be formed.

2. The pulp-strips are subjected to the action of press-rolls for the gradual removal of water and progressive solidification of the fibrous aggregate; it is then further dried by heat on a steam-heated cylinder; and then wound up in what is termed a magazine roll, which thus holds a series of discs in close contact. These are detached as required for the further operation of twisting, and are disposed for winding off in a horizontal or inclined position beneath the spindles.

3. The winding off and twisting involves the passage through the machine which is the subject-matter of patent No. 4 (*ante*) from which the strips are delivered continuously to the spindles. These have a speed of 3,000 to 8,000 revolutions per minute, with the sliver travelling at 8 to 16 metres per minute, according to the size of the yarn and the degree of twist required.

The following table of results of tests of tenacity and "elasticity" more particularly illustrates the technical features of the wood-pulp "spinning" systems:—

	Metrical count.	Breaking strain in terms of breaking length.	Extensibility per cent.
Silvalin strips (dry) .	2,891	2,390	3·06
,, yarn . . .	2,900	4,810	6·44
Altdamm (Türk) strips .	13,153	4,170	2·84
Strips rounded (sliver) . .	8,222	5,014	2·24
,, ,, ,, .	8,408	5,187	2·71
Finished yarn . .	12,100	6,413	3·06

From his extended investigations of these products Prof. Pfuhl concludes that this class of yarns made from pure wood-cellulose have a mean breaking length of 5 to 7 km. with an extensibility of 6 to 7 per cent.; and these constants define a textile quality sufficiently high for their utilisation under the ordinary conditions of wearing, both as warp and weft. The warps of wood-pulp yarns require no previous "dressing" or sizing. The finished fabrics, it may be mentioned, have about one-half the strength of jute fabrics of the same make and weight. In regard to the conditions of utilisation of such fabrics, it is to be noted that, when wetted, they lose their tensile quality entirely; and although they regain their strength in drying, it is evident that the defect in question is a serious limitation of their utility.

(b) *Cost of Production of Silvalin Yarns.*—The estimates of Prof. Pfuhl are based upon a daily output of 6,000 kg. or 1,800 tons per annum, involving 2,160 spindles running eleven hours; the corresponding production of sliver-strips running continuously, *i.e.*, twenty to twenty-four hours per day. In the estimates, the production of a No. 3 (metrical) yarn is considered. The capital outlay is summarised as follows:—

	Marks.
Site and land, 15,000 kr....	15,300
Buildings, 2,000 mr., etc.	71,400
Machinery and plant	309,500
Business capital	126,800
	523,000

These represent an annual charge of about 36,000 m. and adding salaries the establishment represents a charge of

56,807 m. per annum. Wages are estimated at 60,320 m., and coal (at 20 m.) 43,160, adding for lighting, packing, etc., 41,000 m. The total annual charge is 201,287 m. This on the basis above set forth gives a cost of production per ton of 111·83 marks. Adding 20 marks for one patent licence, we have a total cost of 131·83 marks. Comparing these costs with those of spinning jute to yarn of the same count, which was estimated at 100 to 120 m. under similar conditions, it is seen that they are some 10 to 20 per cent. higher. The respective raw materials have now to be brought into account, viz., sulphite cellulose at 15 to 18 m. per 100 kg., and jute at £10 to £14 per ton. The final comparison is made in the following terms:—

		Marks for 100 kilos.	
Total cost of production	Jute warp yarn, No. 6...	34	43
	Jute weft yarn, No. 5, 4	31	39
	Silvalin yarn, No. 5, 5...	28	32

Physical Properties and Application of Wood-pulp Yarns and Fabrics.—It has already been indicated, and is, in fact, more or less self-evident that wood-pulp yarns are limited in their utility. In measuring the utility a number of general principles have to be taken into account as well as the practices and conventions of the textile industry which follow from them. The numerical basis of measurement or the "counts of yarn" is the $\frac{\text{weight}}{\text{length}}$ relationship, which in the textile industry takes a number of conventional forms. The trade in coarse yarns which alone come into consideration here, is mainly concerned with flax, hemp and jute or bast fibre yarns, and low grades of cottons. Thus we have the English units or yarn numbers for bast fibre yarns = the number of leas (of 300 yards) in the pound; for cottons the number of hanks (of 840 yards) in the pound. The jute trade (Dundee) takes an inverse measure in terms of the "spindle" of 14,400 yards, the number of pounds in this length being the yarn number. For wood-pulp yarns the simpler metrical numeration obtains, viz., the number of metres (unit of length) to the gram (unit of weight). The following table, of the metrical yarn numbers and their equivalent in the conventional units will be found useful.

Table of equivalent yarn "numbers" or $\frac{\text{weight}}{\text{length}}$ description compared with metrical counts.

Metrical counts: metres per 1 grm.	Cotton count: n. (840) yds. per lb.	Flax counts: n. (300) yds. per lb.	Jute counts: lbs. per 14,400 yds.
1·0	0·691	1·654	29·0
1·693	1·0	2·800	17·1
0·605	0·357	1·0	48·0
29·0	17·1	48·0	1·0

The strength or "tenacity" of yarns is determined as a breaking-strain, but usually expressed as a breaking-length, that is, the length of the breaking-weight of the yarn itself. This is comparable at once with the sectional breaking-strain usually applied to solid substances. For where L expresses breaking-length, s specific gravity, and k the breaking-strain per 1 mm. of sectional area, $L \times s = k$.

Breaking-Length.—It is an expression which eliminates two of the three dimensions, that is, it is independent of the sizes of yarns or threads, as of the thickness or width of fabrics such as paper produced in sheet or web. It will be noted as a conventional expression, but of very great "convenience," and gives a comprehensive or aggregate expression of tensile quality, and thus is applicable to the most diverse substances and in their most varied form.

Fracture of a textile yarn or paper is accompanied always by elongation under the strain; this of course is a certain measure of true elasticity. The latter would be defined as the amount of extension of which the fabric is capable, with the condition of reverting to its former dimensions when the strain is removed. This quality, however, is seldom defined or tested in textile fabrics.

Extensibility is usually expressed as the total percentage elongation sustained at or under the breaking-strain.

The following table of these quantities applies to the most important textiles.

		Breaking Length. Kilometres.	Elasticity.
Mean averages for Commercial Products.	Cotton yarns	13—14	3·97
	Ramie yarns	11—12	0·8—1·8
	Flax yarns, wet spinning ..	12·4—19·5	1·1—1·8
	Flax and tow yarns, dry spinning	11·8—12·4	2·5—3·7
	Jute yarns	9·9	2·0
	Lustra cellulose average ..	12·0	2·0
	Artificial silks, extremes ..	8·0—14·0	7·0—18·0

The mechanical properties of papers are expressed in the same terms, and it is interesting to compare the range of numbers for the highest classes of papers:—

	Breaking Length. Metres.	Elongation. Per cent.
Rag papers, Manila papers and wood pulp papers (air dry) ...	4,000—8,000 ...	3·8

It is evident from these numbers that the shorter units common to papers produce a texture approximating in mechanical properties to the lower grades of spun yarn.

From the preceding *exposé* it would appear that inventors have endeavoured to overcome the unfitness of paper as such for textiles, or weaving uses, by changing the form and usual dimensions of the web of paper. The stages in the productions of a cylindrical product or yarn are (1) cutting, (2) rolling and (3) subjecting the cylindrical rolled strips to a twisting process whilst in a moist condition. The effects of these treatments in increasing the solidity and resistance of the agglomerates is shown by the following figures:—

	Breaking Length. km.[1]	Elongation. Per cent.
Plane strips, dried	4·17	2·84
Rolled into cylindrical form	5·18	2·71
Rolled and twisted	6·41	3·06

The following numbers have reference to wood-pulp yarns as industrially prepared:

Silvalin (Kron process, 1903—4):		
Mean of 240 tests	5·498	6·8
Maximum observed	8·314	10·5
Minimum observed	4·10	2·9
Altdamm (Türk process, 1903—4):		
Mean of 90 tests	6·159	7·71
Maximum observed	7·695	11·16
Minimum observed	3·619	4·38

As a chemical individual wood cellulose differs but little from cotton cellulose; and when only chemical relationships are involved, there is an obvious probability of the former being able to substitute cotton as a basis of manufacture.

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[1] Km. is the contraction for kilometre.

For such substitution there is always the inducement of relatively low market price.

SPECIAL CELLULOSE INDUSTRIES.

There are several important industries which have been developed upon the characteristic properties of derivatives of cotton cellulose. The modern industry of high explosives is based upon the nitric esters of cotton, which in certain cases are associated with the corresponding nitrates of glycerine. As shown in Chapter II. cotton can be nitrated, that is, combined with nitric acid by simple methods and without any evident structural change. The nitro-cotton, or gun cotton, has the external appearance of ordinary cotton, but is harsher to the touch, and the addition of the large weight of 70 or 80 per cent. due to the combination with nitrate groups, causes minor structural changes which can be well observed under the microscope.

The properties of gun cotton are primarily those associated with rapid or explosive combustion; combination with the nitric groups introduces so much oxygen into the molecule that the new compound has all the elements or internal conditions for complete combustion, whereas ordinary combustion depends upon the gradual supply from without of atmospheric oxygen to the burning body. When gun cotton is fired, there is a rapid propagation of the combustion, and when this takes place in an enclosed space detonation occurs, with rupture of any containing vessel, due to the enormous development of gas[1] at high temperature.

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[1] The products of explosion of the nitrate are represented by the equation $2\ C_{24}H_{18}O_9\ (NO_3H)_{11} = 24\ CO + 24\ CO_2 + 17\ H_2 + 12\ H_2O + 11\ N_2$ and the heat evolved is 2,200 calories per 1 gramme.

The cotton nitrates are soluble in a number of organic liquids in which they swell up and pass into homogeneous solution; with limited proportion of such solvents, and mechanical means, the fibrous nitrates may be worked up into structureless plastic masses, which can be drawn or moulded into threads or rods, or rolled into sheet. It is an important discovery that glycerine or nitro-glycerine is a solvent of nitro-cellulose. Nitro-glycerine resembles nitro-cotton in fundamental combustibility, and is similarly a high or blasting explosive, even more powerful than nitro-cotton, owing to the somewhat higher relative proportion of oxygen. It sounds like a paradox that on bringing these two high explosives together a mixture results which has the properties of restrained combustion, or regulated explosion. These bodies worked together in suitable proportions produce a plastic mass which can be drawn, as above stated, or shaped. When flame is communicated, there is a regulated combustion proceeding from the external layers to the centre of the mass. Explosives of this order can, in fact, be used as propulsive explosives, that is for military ammunition; the ordinary forms are cordite, balistite, etc.

It would appear to be possible to replace cotton for the manufacture of nitro-cotton by the wood celluloses, but there are many reasons, partly of constitution, and partly having to do with the external characteristics or fibrous forms, which have prevented this from taking any deep root, and we can therefore hardly enter into the specialised technology of gun cotton and explosives as a development of wood-pulp industry.

The same may also be said of the very important industry in articles known as celluloid, xylonite, etc. This art and industry is based upon the plastic qualities of nitro cellulose when treated with suitable solvents, and the plastic mass obtained by incorporating the fibrous nitrates with special solvents and completing the mixture to a homogeneous mass by means of mechanical appliances, can be shaped into any required form. There are particular reasons why this industry also has not availed itself of the supplies of wood cellulose of which the market value is approximately one-third that of the forms of cotton which are ordinarily used.

These reasons, as previously indicated, are partly in the relative inconvenience of handling the short fibres of the wood celluloses: and partly from the particular features of instability characterising compounds which are potentially self-destructive. Gun cottons and the lower nitrates of cotton are "unstable" as originally produced owing to the presence of sulphuric acid residues in combination. These are eliminated by exhaustive washings and successive boilings with water. When so purified and "sterilised" they may be kept for prolonged periods without change.

But other celluloses are constitutionally differentiated from the normal cotton cellulose, and contain a proportion of groups of less intrinsic stability: these nitrated to the same degree are correspondingly less stable, and liable to spontaneous decomposition. Hence a lower stability of the entire complex and unsuitability for these industrial uses.

Cellulose Acetates.—The highly combustible and explosive nature of the cellulose nitrates imports a considerable danger in the manufacture and use of celluloid or xylonite. An important use of the nitrates is for the manufacture of photographic films, and in ordinary use this has not led to any serious catastrophe. On the other hand, the film employed to carry the photographic picture in the kinematograph, the picture being projected on to a screen by means of powerful illuminants, is a combination of risks, which has led to several disasters. It is a well-known objective of inventors to discover an efficient substitute for the nitrate. Cellulose acetate is an ester of cellulose which is a close analogue of the nitrate, is also soluble in organic solvents, and may be shaped in admixture with these in any desired way. The first serious attempts to prepare the cellulose acetate on the industrial scale date from 1890. It was found by ourselves that certain forms of cellulose can be brought into reaction with acetylating reagents in presence of zinc acetate, and such process was carried out on an industrial scale.

Further investigations of other chemists led to the observation that cellulose combines readily with acetic anhydride in presence of sulphuric acid relatively in small quantity, and taking part only in determining the main reaction. Such a process, the subject of a series of patents by Lederer (*see* p. 240), has led to considerable economy in the production of the acetate, and the matter is being industrially developed in one or two countries. The acetate film answering all the requirements of photographic use is still, however, in the embryo stage of development.

Owing to the simplicity of the reaction and the relative inertness of acetyl groups, there is every reason why the wood celluloses should answer all requirements for this industry. The reaction is usually carried out with a mixture of glacial acetic acid and acetic anhydride in equal proportions to which the calculated small quantity of sulphuric acid is added (Lederer); in contact with this reactive mixture, the celluloses are gradually and progressively attacked and pass into solution: Low temperatures only are required, and 50° C. is the general maximum. The product is obtained as a highly viscous liquid, that is, a solution of the ester in the excess of the reactive mixture. The mixture is treated with water, which precipitates the ester, and, by suitable mechanical means, this is effected in a state of minute subdivision of the ester, so that it is easily washed. When dry it dissolves to bright solutions in its special solvents, which are chloroform, ethylene chlorides, acetic acid, phenol, etc. It is to be noted that these solvents present difficulties in use, and they are by no means so convenient as the solvents used for the nitrates. Variations of the process, however, have led to the production of acetates soluble in acetone, a solvent which is free from objection in use.

An important question of cost necessarily enters as determining the extent of application of these bodies. Owing to the relative high price of acetic anhydride, and the necessity of using an excess of reaction mixture, the costs of acetate obtained as above described is relatively high. In employing solvents, which are lost in the working of the acetate to particular forms, the cost is added to.

Whereas cellulose nitrates can be bought in the open market at from 1*s*. to 2*s*. per lb., the acetates stand at a multiple of these figures, viz., 6*s*. to 9*s*. a lb.

It is evident that such prices exclude applications save such as are relatively independent of cost.

Another point to be noted in connection with these acetates is that while the reaction is direct, and, in one sense, simple, there is no doubt that the use of acid catalysts brings about the breaking down of the cellulose aggregate by hydrolytic change, from which results a loss of structural properties. The acetates so produced and converted into continuous solids are relatively brittle.

Processes which overcome these objections depend upon the use of neutral or saline catalysts, such as zinc chloride. These appear to determine the ester reaction under conditions which do not involve hydrolysis or, at least, involve it to a much less extent. The products of such reactions are what may be considered the normal series of acetates. The reaction of cellulose with acetic anhydride in the presence of zinc chloride as catalyst, and glacial acetic acid as diluent can be observed through a remarkable series of gradations up to the extreme or maximum point. If cotton is used, or more particularly cotton yarn, it is easily seen that the lower acetates are formed without any sensible modification of the cellulose or yarn. Acetyl groups may be introduced into the cellulose molecule with an increase of weight up to 26 to 36 per cent., producing an acetylated derivative unchanged as to form, showing certain new properties in respect of lower attraction for atmospheric moisture, and for those colouring matters which dye cotton directly. When carried to higher stages, the further introduction of acetyl groups cause a notable swelling of the cellulose, and, finally, as the stage of tri-acetate is reached, the product passes into solution. This method of acetylation is economical by reason of the fact that there is a very high utilisation of the acetic anhydride.

A further point of economy arises in the application of the acetate, since for certain purposes the reaction mixture itself can be employed. This avoids the process of separation of the ester, in which the solvent is lost, or so diluted as to have a much depreciated value; and, moreover, the separated ester requires again to be treated with solvents, which become an added cost. These difficulties, which appear of small magnitude, have effectually impeded the development of the applications of the product. A general bibliography on the subject since 1895 will indicate the directions in which specialists may inquire for evidence of the influence of these difficulties on the evolution of this cellulose ester.

General Bibliography of Cellulose Acetates.

Original papers.

	Schutzenberger and Waudin.	*Comptes Rendus*, 68, 814.
	Franchimont.	*Berl. Ber.* 12, 2059.
	Cross and Bevan.	*Journ. Chem. Soc.* (1890), 57, 1.
1905	Cross, Bevan and Briggs.	*Berl. Ber.*, 38, 1859, 3531.
	Haeussermann.	*Chem. Ztg.*, 29, 667.
1906	Ost.	*Zeitsch. Angew. Chem.*, 19, 993.
1907	Berl. and Watson Smith.	*Berl. Ber.*, 40, 903.
1908	,, ,,	*Journ. Soc. Chem. Ind.*, 534.
	F. Beltzer.	*Mer. Sci.*, 22, 648.
	Knoevenagel.	*Chem. Zeit.*, 32, 810.
1895-1905	Cross and Bevan.	“Cellulose.” “Researches on Cellulose,” I., “Researches on Cellulose,” II.

The following patents.

1894	Cross and Bevan.	E. P. 96761.
1900	Lederer.	E. P. 11749.
1902	Landsberg.	E. P. 4886.
,,	Lederer.	E. P. 7088.
,,	Boesh.	U. S. P. 708457.

1903	Miles.	U. S. P. 733729.
,,	Farbenf. Elberfeld.	U. S. P. 734123.
,,	,,	U. S. P. 738533.
,,	Balston and Briggs.	E. P. 10243.
,,	F. Bayer & Co.	E. P. 7346.
1904	Lederer.	U. S. P. 774677.
,,	Badische, A. S. F.	F. P. 347906.
1905	Miles.	E. P. 19330.
,,	Fabr. Prod. Chim. Flora.	E. P. 9998.
1906	Akt. Ges. f. Anilin.	E. P. 1939; F. P. 362721, 368738.
,,	Farbenf. Elberfeld.	U. S. P. 809935.
,,	Corti.	U. S. P. 816229.
,,	Lederer.	E. P. 19107, 26502.
,,	,,	F. P. 368766, 371357.
,,	F. Bayer & Co.	F. P. 371447.
,,	Knoll.	F. P. 369123.
,,	Badische, A. S. F.	U. S. P. 373994, 812098.
1907	Lederer.	E. P. 3103.
,,	,,	F. P. 374370.
,,	Fischer.	D. R. P. 201907.
,,	Knoll.	E. P. 2026, 2026A, 2026B.
,,	,,	F. P. 373994.
,,	,,	F. P. 383636.
,,	Benne.	D. R. P. 210519.
,,	Soc. Anon. Explosifs.	F. P. 385179.
1908	Lederer.	U. S. P. 902093.
1909	Knoll.	U. S. P. 891218.
,,	,,	E. P. 7743.
,,	Donnersmarck, K. A. W.	U. S. P. 922340.
,,	,,	F. P. 400652.
,,	Lederer.	E. P. 11625.

The derivatives above described are themselves esters or compounds of cellulose and acid groups, and are treated or manipulated as such. Thus, the solutions of both the nitrate and acetate can be drawn or spun to a thread, which, when sufficiently fine, is an artificial silk. The nitrate is the basis of the earliest, and still very successful, method of producing these artificial textiles, nitro-cellulose is only a stage in a cycle of industrial operations. The nitrate is readily *denitrated*, that is, its nitro groups may be removed with regeneration of cellulose. The earlier forms of artificial silks were not so treated, or, at least, only partially denitrated, and therefore were necessarily highly combustible, if not explosive. This property very considerably prejudiced the earlier attempts at utilising them: this form has, however, given way to the denitrated or cellulose product, which is now an ordinary staple textile. The acetate in the form of thread or artificial silk could be used as such, as it is not more combustible than ordinary cotton. It is a product, however, that is still only an industrial curiosity, and has not taken any prominent position, probably owing to the cost of production of the original acetate which, for the reasons given, is necessarily high. A further difficulty in the same direction is the added cost of redissolving the products in solvents, which are lost during the spinning process. There appears to be, however, a prospect of producing a thread to compete with the artificial silks already established, by spinning or drawing the original reaction mixture in the case of the normal series of acetates.

We have already described a peculiar compound of cellulose, which resembles the above in being formed by combination of cellulose with acid groups; but the compound is soluble only in alkaline liquids, and, moreover, is unstable, that is, decomposes spontaneously with reformation of cellulose. This compound is the sulpho-carbonate, or xanthogenic ester of cellulose, generally known as "Viscose." This compound was described briefly in an early chapter, and its capabilities of regeneration in structural modifications were indicated. Viscose has been used in a number of industrial applications, all of which depend upon this essential property. (1) In thread or yarn, it is an artificial silk. (2) In plane or sheet form it is a transparent film. (3) Solidified in masses it is a solid, which, when dried, can be shaped or turned in the lathe to any required form. The cellulose can also be mixed with solid bodies in preparing mixed agglomerates in which the structural qualities of the cellulose as the binding or agglomerating medium assert themselves, even when diluted with large proportions of foreign inert matters. (4) In less definite forms, but exerting the same technical effects, viscose is used in sizing paper and textiles, and for various other applications.

For the general reasons above stated these industries are not necessarily connected with wood pulps, since they are more generally applications of cellulose. As a matter of fact, however, the wood pulps are a most convenient form of cellulose for the manufacture of viscose, and we may therefore give a few particulars in elucidation of these newer developments.

The first stage in the "viscose process" is the conversion of the cellulose into alkali cellulose by treatment with caustic soda solution at mercerising strength (15·0—20·0 per cent. NaOH).

The limits of composition of this product are

	Per cent.
Cellulose	25—30
Caustic soda (NaOH) . .	12·5—15
Water	62·5—55

There are two methods of treating the wood pulp (cellulose) with the alkaline lye. The first is to reduce the wood pulp in a kollergang with sufficient water to bring about the disintegration of the sheets, and then add the calculated quantity of caustic soda dissolved in such a quantity of water as to produce a mixture of the above composition.

The second method is to steep the sheets in excess of a lye of 17·5 per cent. NaOH, lift, drain from the excess, press to a calculated weight, and then grind in a kollergang or mixer to secure even incorporation of the mercerising reagent with the cellulose.

The alkali-cellulose is a voluminous semi-dry mass resembling bread-crumbs in appearance. It can be stored in masses without change of composition by drainage.

The alkali-cellulose is protected during storage from access of atmospheric air—that is from the action of atmospheric carbonic acid.

The second stage in the process is the reaction of the alkali-cellulose with carbon bisulphide. This takes place spontaneously at ordinary temperature. It is important to carry out the reaction in a closed vessel to prevent loss of the very volatile bisulphide. The vessel ordinarily used is of the form and construction of a churn. In dealing with large masses it is found of advantage to replace the simple barrel or cylinder by a vessel of hexagonal or octagonal form. The charge of alkali-cellulose having been introduced, the quantity of bisulphide is poured upon the mass, the vessel closed at the man-hole and slowly rotated, to secure even admixture and distribution of the contents.

The reaction is attended with a rise of temperature of 3 to 7° C. according to the mass, initial temperature and other conditions of reaction. The mass changes in colour to yellow, and the action is arrested at the moment that it begins to lose its voluminous free condition.

The completed product tends to agglomerate, and for the purpose of making a solution it is important that this should be stirred into water before the stage of agglomeration is reached.

There are in fact two ways of working up the xanthate: the first is by the action of water to a solution of 10 to 12 per cent. cellulose strength, the second, the agglomeration is completed by the action of heavy masticating rollers, such as are used in the manipulation of indiarubber.

The latter method is, however, only used in connection with the making of solids which are shaped into cylindrical form as a stage in the preparation of the solids known as viscoid or viscolith.

The viscose solution is the starting point for the preparation of artificial silk. For this industry the crude solution is subjected to filtration which requires to be of a very searching kind. In spinning or drawing the silk the solution has to pass through orifices of fine dimensions, 0·1 to 0·15 of a millimetre, and hence it is important to eliminate all residues of insoluble matter.

The xanthate or soda salt of cellulose xanthogenic acid is the basis of viscose. It is accompanied by by-products of the original reaction and moreover, as it tends to spontaneous decomposition by interaction of the alkali with the sulpho-carbonic residues in combination with the cellulose, there is an accumulation of these by-products at the expense of the xanthates, which hold a steadily diminishing proportion of the characteristic group. The spontaneously diminishing ratio of these groups to the cellulose is attended by diminishing solubility of the cellulose complex.

Further, the by-products are soda salts of the carbonic and sulpho-carbonic series, and are precipitants of the cellulose compound. In both directions therefore there is a tendency for the viscose to revert to the solid state.

A solidified viscose is a coagulated xanthate, and may be washed in water, and then redissolved in caustic soda solution.

The final stage in the reversion is *cellulose* itself, which is reached only after prolonged periods at ordinary temperatures.

These phenomena are made use of in several of the applications of viscose, as in the engine sizing of paper and the sizing and finishing of textiles. The decomposition is hastened by the interaction of the soda salts with salts of zinc or magnesia, and these are employed in the process of paper sizing.

Another characteristic decomposition is that determined by salts of ammonia. Viscose in contact with sulphate of ammonia in solution interacts quantitatively; the soda is converted into sulphate and is replaced by ammonia (base) in both the by-products and the xanthate. These ammonia compounds are extremely unstable, and therefore there is a very rapid decomposition of the xanthate to cellulose (hydrate). This reaction is the basis of one of the methods of spinning or drawing to artificial silk.

Another method which also fulfils requirements of the spinning process, is that of treatment with acids, which bring about a still more rapid decomposition.

Notwithstanding the rapidity of action the cellulose hydrate adapts itself perfectly, and shows the same continuity of substance and resistant quality as in the case of the saline baths.

In regard to mechanical methods, these are two, in principle and detail. 1. The solution is projected from a fine glass tube: each individual thread is thus formed apart, and a certain number of these are united into a compound thread by passing through a glass loop in the coagulating or decomposing bath.

The compound thread with its 14 to 18 elements is manipulated in the untwisted state, in the first instance; at a later stage, as a special operation, it receives the twist of 100 to 200 per metre.

An ingenious method of combining these operations is the centrifugal spinning box of Stearn and Topham.

This is a box of special construction rotating at a high rate of speed on a vertical axis. In this case the compound thread is directly produced in the coagulating bath by projecting the viscose through a plane cap or nozzle of platinum perforated with 14 to 18 holes. Each hole contributes a thread, and these are drawn forward in the coagulating bath as a compound thread, which ascends and is taken vertically up and down over a glass roller to fall into a funnel which communicates with the rotating box. The centrifugal motion has the effect of drawing the thread forward, twisting it, and laying it peripherally in the box as a hollow or annular cocoon.

The hydrated thread in this "cake" form is removed from the box at intervals, re-wound into skeins and further manipulated for purification of the cellulose.

The industrial applications of viscose necessarily involve a multiplicity of detail both chemical and mechanical. Chemically, the product is difficult to handle by reason of its alkalinity and the large proportion of derivative sulphur containing groups which are characteristic of the product and by-products.

When these are decomposed, the products are sulphuretted hydrogen and other odorous derivatives.

When the decomposition takes place spontaneously, the alkaline reaction being maintained, the products are carbon bisulphide and traces of other sulphur derivatives.

The mechanical difficulties of handling viscose are largely a question of materials, that is, of materials having the power of resisting the attack of the associated products whether in the original condition or under the condition of decomposition by the reagents above indicated.

It would be outside the scope of this work to deal with these matters in detail.

A large number of inventions dealing with these methods and details have grouped themselves around the original invention, which dates from 1892. These inventions and developments are so numerous that they form the subject of a monograph of 127 pages, with 88 pages additional, devoted to the patent literature. We give the title of this work in full: "Die Viscose—ihre Herstellung, Eigenschaften, and Anwendung," von Dr. B. M. Margosches in Brunn. Leipzig. L. A. Klepzig.

This monograph is extensive, and in fact complete, and it is therefore unnecessary to duplicate this contribution to technical literature.

In the course of discussions in this and preceding sections, we have not dealt directly with the commercial aspects of the wood pulp industries nor with the subject of their money or selling values. These involve questions of minute detail, and a special aspect of these industries outside the scope of the present work.

But we may deal in a very broad and general way with these values, as an illustration of an important principle of technology, that is, the appreciation of value of a raw material worked up by the agencies of chemical reagents, coal and steam, and manual labour, into a finished manufactured product.

The German language, we may note in passing, provides the apt term "*vered(e)lung*" which means literally "ennobling," for this process of adding value to raw materials and the special term connotes the general idea and aim of manufacturing industry. *We* have to borrow a Latin equivalent, and this suggests that the idea of "appreciation" is somewhat of an exotic.

However the associated ideas may be expressed and assimilated the facts are equally striking and interesting, and in the case of the cellulose industries they may be stated in the form of an ascending scale of related values as follows:—

	£	*s.*	*d.*
(a) 1 cubic metre of wood weighs 400—500 kilos. and is worth in the forest, say . .	0	3	0
(b) Used as fuel it has a "burning" value, say	0	6	0
(c) As mechanical wood pulp it is worth, say .	0	7	6
(d) Treated by the bisulphite or alkali process it would yield 150 kilos. of pulp, say .	0	15	0
(e) Transformed into paper the pulp or cellulose is worth, say	1	15	0

	£	*s.*	*d.*
(f) Transformed into wood pulp yarn, it is worth, say	2	5	0
(g) Transformed into artificial silk or lustra cellulose, it is worth, say[1] . . .	7	10	0

These figures cannot be stated more exactly, that is, represent actual selling values; but fractional variations would not affect the general scale of values which mounts in multiples from 1 to 50. Specialists are aware that these achievements in "veredlung" by no means exhaust the possibilities of cellulose technology and industry.

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[1] This interesting industrial record we owe to Dr. O. Witt and Max Müller.

CHAPTER XI

SPECIMEN PAGES—VARIOUS TYPES OF PAPER

This chapter embodies specimen sheets of paper selected as types, with a description of their characteristics. The selection is designed to bring out the position of wood pulps, in their various forms, as staple paper-making raw material.

In establishing this position there have been, of course, the two elements of competition: first, technical effect; and second, cost.

As a result of the competition, the wood pulps have largely displaced cotton, jute and esparto. The general result of their introduction has been to cheapen production, with no sensible lowering of general quality.

It is unnecessary again to point out that ground wood or "mechanical" wood pulp has many undesirable characteristics, and, of course, it is rigidly excluded from papers for documents of permanent value.

But even this "Cinderella" fibre has proved of great practical importance and utility, in enabling papers to be produced at a cost commensurate with the enormous demand for cheap publications.

The careful comparison of these papers, with attention to the full specification of characteristics printed on each sheet, will enable the reader to draw his own conclusions as to the extent to which wood has vindicated its present position as of first-rate importance.

Specimen Paper. No. 1.

Trade Description.

Heavy Imitation Art. 46 lbs. Demy = 480 sheets.
(Messrs. Spalding & Hodge.)
Price 2⅝d. per lb.

RESULTS OF TEST.

Weight of Ream.		
Demy 17½″ × 22½″ = 480 sheets	46 lbs.	
Grammes per square metre ...		171·1 gms.
Thickness.		
Single sheet	·0058 ins.	·147 mm.
Strength.		
Tensile strength on strips 15 mm. wide (Leunig's machine)		
Machine direction 14·1 lbs.		
Cross direction 9·3 lbs.		
Mean tensile strength of paper	11·7 lbs.	5·32 Kilos.
Breaking Length	2269 yds.	2073 Metres.
Breaking Weight per sq. mm. of Sectional Area		2413 gms.
Loss of Strength due to Folding.		
On folding 4 times mean % loss	51·3%	
On folding 12 times mean % loss	65·0%	
Bursting Strain.		
Lbs. per square inch required	24·0 lbs.	
Grammes per square centimetre		1687 gms.
Ash.		
Percentage of loading	30·4%	
Fibrous Composition.		
Esparto	80%	
Sulphite Wood	20%	

Volume Composition.

Grammes per c.c.			Percentage composition by volume.		
Paper	Fibre	Ash	Fibre	Ash	Air space
1·163	·809	·354	53·9	14·2	31·9

SPECIMEN PAPER. No. 2.

Trade Description.

High-class Rag Paper. 26 lbs. Demy = 480 sheets.
(Messrs. Wiggins, Teape & Co.)
Price 7¾d. per lb.

RESULTS OF TEST.

WEIGHT OF REAM.			
Demy 17½" × 22½" = 480 sheets		26 lbs.	
Grammes per square metre ...			96·7 gms.
THICKNESS.			
Single sheet		·0042 ins.	·107 mm.
STRENGTH.			
Tensile strength on strips 15 mm. wide (Leunig's machine)			
Machine direction	18·7 lbs.		
Cross direction	12·1 lbs.		
Mean tensile strength of paper		15·4 lbs.	7·03 Kilos.
BREAKING LENGTH		5287 yds.	4830 Metres.
BREAKING WEIGHT PER SQ. MM. OF SECTIONAL AREA			4379 gms.
LOSS OF STRENGTH DUE TO FOLDING.			
On folding 4 times mean % loss		5·8 %	
On folding 12 times mean % loss		13·6 %	
BURSTING STRAIN.			
Lbs. per square inch required		45·5 lbs.	
Grammes per square centimetre			3200 gms.
ASH.			
Percentage of loading		2·6%	
SIZING.			
Percentage of gelatine ...		4·16%	
FIBROUS COMPOSITION.			
Cotton		100%	

VOLUME COMPOSITION.

Grammes per c.c.				Percentage composition by volume.			
Paper	Fibre	Ash	Gelatine	Fibre	Ash	Gelatine	Air space
·904	·844	·023	·037	56·3	0·9	2·7	40·1

SPECIMEN PAPER. NO. 3.

Trade Description.

Sulphite Printing. 21 lbs. Demy = 480 sheets.
(Messrs. Lepard & Smith.)
Price 2¼*d.* per lb.

RESULTS OF TEST.

WEIGHT OF REAM.		
Demy 17½″ × 22½″ = 480 sheets	21 lbs.	
Grammes per square metre ...		78·1 gms.
THICKNESS.		
Single sheet	·0033 ins.	·084 mm.
STRENGTH.		
Tensile strength on strips 15 mm. wide		
Machine direction 7·4 lbs.		
Cross direction 2·5 lbs.		
Mean tensile strength of paper	5·0 lbs.	2·27 Kilos.
BREAKING LENGTH	2125 yds.	1938 Metres
BREAKING WEIGHT PER SQ. MM. OF SECTIONAL AREA		1800 gms.
LOSS OF STRENGTH DUE TO FOLDING.		
On folding 4 times mean loss	34·0 %	
On folding 12 times mean loss	40·0 %	
BURSTING STRAIN.		
Lbs. per square inch required	9·5 lbs.	
Grammes per square centimetre		668 gms.
ASH.		
Percentage of loading	22·0 %	
FIBROUS COMPOSITION.		
Sulphite wood	100 %	

VOLUME COMPOSITION.

Grammes per c.c.			Percentage composition by volume.		
Paper	Fibre	Ash	Fibre	Ash	Air space
·929	·725	·204	48·3	8·2	43·5

SPECIMEN PAPER. No. 4.

Trade Description.

Imitation Art. 22 lbs. Demy = 480 sheets.
(Messrs. Lepard & Smiths, Ltd.)
Price 2⅝*d.* per lb.

RESULTS OF TEST.

WEIGHT OF REAM.		
Demy 17½" × 22½" = 480 sheets	22 lbs.	
Grammes per square metre ...		81·8 gms.
THICKNESS.		
Single sheet	·0030 ins.	·076 mm.
STRENGTH.		
Tensile strength on strips 15 mm. wide (Leunig's machine)		
Machine direction 9·4 lbs.		
Cross direction 4·7 lbs.		
Mean tensile strength of paper	7·1 lbs.	3·23 Kilos.
BREAKING LENGTH	2880 yds.	2633 Metres.
BREAKING WEIGHT PER SQ. MM. OF SECTIONAL AREA		2834 gms.
LOSS OF STRENGTH DUE TO FOLDING.		
On folding 4 times mean loss	54·9 %	
On folding 12 times mean loss	69·0 %	
BURSTING STRAIN.		
Lbs. per square inch required	15·1 lbs.	
Grammes per square centimetre		1055 gms.
ASH.		
Percentage of loading	24·2 %	
FIBROUS COMPOSITION.		
Esparto	90 %	
Sulphite wood	10 %	

VOLUME COMPOSITION.					
Grammes per c.c.			Percentage composition by volume.		
Paper	Fibre	Ash	Fibre	Ash	Air space
1·076	·816	·260	54·4	10·4	35·2

SPECIMEN PAPER. No. 5.

Trade Description.

Esparto Printing. 22 lbs. Demy = 480 sheets.
(Messrs. Lepard & Smiths, Ltd.)
Price 2⅞*d.* per lb.

RESULTS OF TEST.

WEIGHT OF REAM.		
Demy 17½″ × 22½″ = 480 sheets	22 lbs.	
Grammes per square metre ...		81·8 gms.
THICKNESS.		
Single sheet	·0034 ins.	·086 mm.
STRENGTH.		
Tensile strength on strips 15 mm. wide (Leunig's machine)		
Machine direction 9·5 lbs.		
Cross direction 5·3 lbs.		
Mean tensile strength of paper	7·4 lbs.	3·37 kilos.
BREAKING LENGTH	3002 yds.	2745 metres.
BREAKING WEIGHT PER SQ. MM. OF SECTIONAL AREA		2613 gms.
LOSS OF STRENGTH DUE TO FOLDING.		
On folding 4 times mean loss	32·4 %	
On folding 12 times mean loss	44·6 %	
BURSTING STRAIN.		
Lbs. per square inch required	17·2 lbs.	
Grammes per square centimetre		1198 gms.
ASH.		
Percentage of loading	17·0 %	
FIBROUS COMPOSITION.		
Esparto	80 %	
Sulphite wood	20 %	

VOLUME COMPOSITION.

Grammes per c.c.			Percentage composition by volume.		
Paper	Fibre	Ash	Fibre	Ash	Air space
·952	·790	·162	52·7	6·5	40·8

SPECIMEN PAPER. No. 6.

Trade Description.

High-class Art Paper. 41 lbs. Demy = 480 sheets.
Prices on application to Messrs. C. Morgan & Co.

RESULTS OF TEST.

WEIGHT OF REAM.		
Demy 17½″ × 22½″ = 480 sheets	41 lbs.	
Grammes per square metre ...		152·5 gms.
THICKNESS.		
Single Sheet	·0052 ins.	·132 mm.
STRENGTH.		
Tensile strength on strips 15 mm. wide (Leunig's machine)		
Machine direction 13·8 lbs.		
Cross direction 7·4 lbs.		
Mean tensile strength of paper	10·6 lbs.	4·85 Kilos.
BREAKING LENGTH	2306 yds.	2114 Metres.
BREAKING WEIGHT PER SQ. MM. OF SECTIONAL AREA		2438 gms.
LOSS OF STRENGTH DUE TO FOLDING.		
On folding 4 times mean % loss	49·1%	
On folding 12 times mean % loss	63·2%	
BURSTING STRAIN.		
Lbs per square inch required	23·3 lbs.	
Grammes per square centimetre		1638 gms.
ASH.		
Percentage of loading	29·0%	
SIZING.		
Percentage of gelatine	5·43%	
FIBROUS COMPOSITION.		
Esparto	45%	
Sulphite Wood	55%	

VOLUME COMPOSITION.

Grammes per c.c.				Percentage composition by volume.			
Paper	Fibre	Ash	Gelatine	Fibre	Ash	Gelatine	Air space
1·152	·755	·334	·063	50·3	13·4	4·7	31·6

SPECIMEN PAPER. No. 7.

Trade Description.
Common Art Paper. 38 lbs. Demy = 480 sheets.
(Messrs. Lepard & Smiths.)
Price 2¾d. per lb.

RESULTS OF TEST.

WEIGHT OF REAM.		
Demy 17½″ × 22½″ = 480 sheets	38 lbs.	
Grammes per square metre ...		141·4 gms.
THICKNESS.		
Single sheet	·0053 ins.	·135 mm.
STRENGTH.		
Tensile strength on strips 15 mm. wide (Leunig's machine)		
Machine direction 11·8 lbs.		
Cross direction 4·8 lbs.		
Mean tensile strength of paper	8·3 lbs.	3·76 Kilos.
BREAKING LENGTH	1950 yds.	1778 Metres.
BREAKING WEIGHT PER SQ. MM. OF SECTIONAL AREA		1858 gms.
LOSS OF STRENGTH DUE TO FOLDING.		
On folding 4 times mean % loss	41·0%	
On folding 12 times mean % loss	48·2%	
BURSTING STRAIN.		
Lbs. per square inch required	18·2 lbs.	
Grammes per square centimetre		1275 gms.
ASH.		
Percentage of loading	28·3%	
SIZING.		
Percentage of gelatine... ...	3·88%	
FIBROUS COMPOSITION.		
Sulphite Wood	90%	
Mechanical Wood	10%	

VOLUME COMPOSITION.

Grammes per c.c.				Percentage composition by volume.			
Paper	Fibre	Ash	Gelatine.	Fibre	Ash	Gelatine.	Air space.
1·047	·710	·296	·041	47·3	11·8	3·0	37·9

SPECIMEN PAPER. No. 8.

Trade Description.

Common News. 14 lbs. Demy = 480 sheets.
Prices on application to Messrs. C. Morgan & Co.

RESULTS OF TEST.

WEIGHT OF REAM.		
Demy 17½″ × 22½″ = 480 sheets	14 lbs.	
Grammes per square metre ...		52·1 gms.
THICKNESS.		
Single sheet	·0041 ins.	·104 mm.
STRENGTH.		
Tensile strength on strips 15 mm. wide (Leunig's machine)		
Machine direction 5·5 lbs.		
Cross direction 2·4 lbs.		
Mean tensile strength of paper	4·0 lbs.	1·81 Kilos.
BREAKING LENGTH	2550 yds.	2324 Metres.
BREAKING WEIGHT OF SQ. MM. OF SECTIONAL AREA		1161 gms.
LOSS OF STRENGTH DUE TO FOLDING.		
On folding 4 times mean % loss	10·0%	
On folding 12 times mean % loss	20·0%	
BURSTING STRAIN.		
Lbs. per square inch required	8·1 lbs.	
Grammes per square centimetre		569 gms.
ASH.		
Percentage of loading	4·2%	
FIBROUS COMPOSITION.		
Sulphite wood	10%	
Mechanical wood	90%	

VOLUME COMPOSITION.

Grammes per c.c.			Percentage composition by volume.		
Paper	Fibre	Ash	Fibre	Ash	Air space
·500	·479	·021	31·9	0·84	67·3

SPECIMEN PAPER. No. 9.

Trade Description.
High-class News. 18 lbs. Demy = 480 sheets.
Prices on application to Messrs. C. Morgan & Co.

RESULTS OF TEST.

WEIGHT OF REAM.		
Demy 17½″ × 22½″ = 480 sheets	18 lbs.	
Grammes per square metre ...		67·0 gms.
THICKNESS.		
Single sheet	·0045 ins.	·114 mm.
STRENGTH		
Tensile strength on strips 15 mm. wide (Leunig's machine)		
Machine direction 6·3 lbs.		
Cross direction 4·1 lbs.		
Mean tensile strength of paper	5·2 lbs.	2·36 Kilos.
BREAKING LENGTH	2578 yds.	2350 Metres.
BREAKING WEIGHT PER SQ. MM. OF SECTIONAL AREA		1378 gms.
LOSS OF STRENGTH DUE TO FOLDING.		
On folding 4 times mean % loss	15·4%	
On folding 12 times mean % loss	19·2%	
BURSTING STRAIN.		
Lbs. per square inch required	11·4 lbs.	
Grammes per square centimetre		808 gms.
ASH.		
Percentage of loading	3·3%	
FIBROUS COMPOSITION.		
Sulphite Wood	80%	
Mechanical Wood	20%	

VOLUME COMPOSITION.

Grammes per c.c.			Percentage composition by volume.		
Paper	Fibre	Ash	Fibre	Ash	Air space
·587	·568	·019	37·9	0·8	61·3

SPECIMEN PAPER. No. 10.

Trade Description.

Bulking Antique Wove Printing. 18 lbs. Demy = 480 sheets.

Prices on application to Messrs. C. Morgan & Co.

RESULTS OF TEST.

WEIGHT OF REAM.		
Demy 17½″ × 22½″ = 480 sheets	18 lbs.	
Grammes per square metre ...		67·0 gms.
THICKNESS.		
Single sheet	·0066 ins.	·168 mm.
STRENGTH.		
Tensile strength on strips 15 mm. wide (Leunig's machine)		
Machine direction 7·7 lbs.		
Cross direction 4·2 lbs.		
Mean tensile strength of paper	6·0 lbs.	2·72 Kilos.
BREAKING LENGTH	2975 yds.	2710 Metres.
BREAKING WEIGHT PER SQ. MM. OF SECTIONAL AREA		1081 gms.
LOSS OF STRENGTH DUE TO FOLDING.		
On folding 4 times mean % loss	35·0%	
On folding 12 times mean % loss	41·7%	
BURSTING STRAIN.		
Lbs. per square inch required	13·1 lbs.	
Grammes per square centimetre		914 gms.
ASH.		
Percentage of loading	7·5%	
FIBROUS COMPOSITION.		
Esparto	95%	
Sulphite Wood	5%	

VOLUME COMPOSITION.

Grammes per c.c.			Percentage composition by volume.		
Paper	Fibre	Ash	Fibre	Ash	Air space
·400	·370	·030	24·7	1·2	74·1

SPECIMEN PAPER. No. 11.

Trade Description.

Cartridge. 29 lbs. Demy = 480 sheets.
(Messrs. Lepard & Smiths.)
Price 2½d. per lb.

RESULTS OF TEST.

WEIGHT OF REAM.		
Demy 17½″ × 22½″ = 480 sheets	29 lbs.	
Grammes per square metre ...		107·9 gms.
THICKNESS.		
Single sheet	·0055 ins.	·140 mm.
STRENGTH.		
Tensile strength on strips 15 mm. wide (Leunig's machine)		
Machine direction 14·5 lbs.		
Cross direction 5·8 lbs.		
Mean tensile strength of paper	10·2 lbs.	4·63 Kilos.
BREAKING LENGTH	3139 yds.	2865 Metres.
BREAKING WEIGHT PER SQ. MM. OF SECTIONAL AREA		2207 gms
LOSS OF STRENGTH DUE TO FOLDING.		
On folding 4 times mean % loss	30·4%	
On folding 12 times mean % loss	40·2%	
BURSTING STRAIN.		
Lbs. per square inch required	19·8 lbs.	
Grammes per square centimetre		1391 gms.
ASH.		
Percentage of loading	9·5%	
FIBROUS COMPOSITION.		
Sulphite wood	99%	
Mechanical wood	1%	

VOLUME COMPOSITION.

Grammes per c.c.			Percentage composition by volume.		
Paper	Fibre	Ash	Fibre	Ash	Air space
·771	·698	·073	46·5	2·9	50·6

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