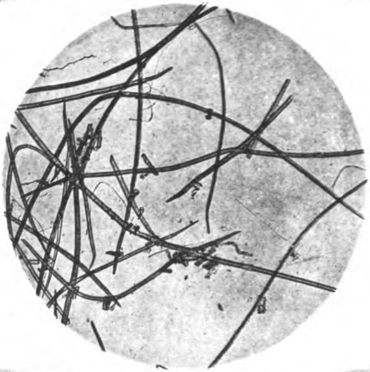
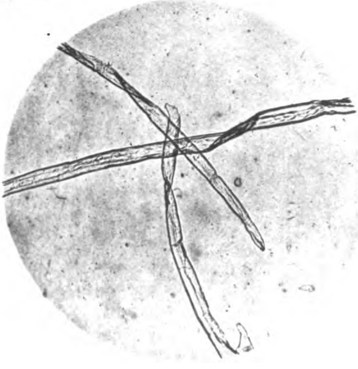
A TEXT-BOOK

OF

PAPER-MAKING





A TEXT-BOOK

OF

PAPER-MAKING

BY

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PREFACE
TO
THE SECOND EDITION.

In preparing this present Edition we have adhered strictly to the original plan and scope of the work, which is that of a text-book of principles, and not either an exhaustive treatise or a minutely descriptive manual of the manufacturing art. We have endeavoured at the same time to bring the matter of the book to the level of later developments, some of which are of such importance as to necessitate the re-writing of certain sections, notably those dealing with the Chemistry of Cellulose and the operations of Sizing, Loading and Colouring. Our aim is to present the subject to the reader according to its scientific perspective; to furnish a guide for the student or apprentice in acquiring his practical experience to the best advantage, and for those who have a working experience of Paper-making, in reviewing either for pleasure or profit, the multitude of facts to be observed in the daily routine of the mill.

We wish to thank our friend Mr. A. D. Little, of Boston, Mass., for permission to make use of his work on 'The Chemistry of Paper-Making'; our thanks are also due to the Publishers of this book, the Howard Lockwood Publishing Company, for the right to reproduce portions of the text.

The Engineering firms of Messrs. Bertram, Ltd., Jas. Bertram and Sons, Ltd., Masson and Scott, Ltd., Mather and Platt, Ltd., have shown their usual courtesy in supplying particulars and drawings of machinery.

To our paper-making friends, more particularly Mr. Thos. Tait and Mr. C. M. King, we are obliged for suggestions and criticisms.

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PAPER-MAKING.

INTRODUCTORY.

Paper-making is essentially a mechanical art, consisting as it does in the production of a continuous web or fabric by aggregating together structural units of relatively minute dimensions.

These, the essential components of paper, are the vegetable fibres, first isolated from the fibrous raw materials by operations of both mechanical and chemical nature, and then further resolved or broken up by mechanical treatment.

But, though the actual paper-making processes are of the mechanical and physical order, they involve auxiliary chemical processes of fundamental importance. Moreover, there is a special chemistry of the fibrous components and of the auxiliary agents used in the making and finishing of papers, to know which is a necessary equipment of the paper-maker.

In presenting this brief outline of first principles, we cannot overrate the importance of a thorough grasp of the composition and constitution of the plant fibres, as the necessary foundation for the intelligent conduct of paper-making, and to this subject we will at once proceed.

Careful study of a mature flowering plant will show that it is made up of structural elements of two kinds, viz. fibres and cells, which, to use a rough parallel, we may liken in function to the bricks and mortar of a house. It is the former which admit of the many extended uses with which we are familiar in the arts of spinning and weaving, and which constitute the fabrics which are the most indispensable to our civilised life. For the most part, as we know, fibres and cells are aggregated together into compound tissues, and a process of separation is therefore a necessary preliminary to the utilisation of the former. The cotton fibre is the only important exception to this general condition of distribution. Here we have the seed envelope or perisperm converted into a mass of fibres, and these, by a spontaneous process accompanying the ripening, so isolated as to be immediately available. Next in order, in point of simplicity of isolation, are those fibrous masses, or tissues, which, although components of complex structures, exhibit a greater cohesion of their constituent fibres than adhesion to the contiguous cellular tissues with which they go to build up the plant. Into such a tissue the "bast," or inner bark layer of shrubs and trees, more especially those of tropical and sub-tropical regions, frequently develops; and it is, in fact, this bast tissue, graduating in respect of cohesion of its constituent fibres, from a close network such as we have spoken of, to a collection of individual fibres or fibre-bundles disposed in parallel series, which supplies the greater part of the more valuable of the textile and paper-making fibres; we may instance flax, hemp and jute, each of which is the basis of an enormous industry. According to the degree of adhesion of the bast to the contiguous tissues, or, in another aspect, according to its lesser aggregate development, so is the difficulty of isolation and the necessity of using processes auxiliary to the mechanical separation of the tissue.

It is worthy of note here that the Japanese paper with which we are in these times so familiar, is prepared by the most primitive means from the bast of a mulberry (*Broussonetia papyrifera*); the isolated tissue, consisting of a close network of fibres, is simply cut and hammered to produce a surface of the requisite evenness, and the production of a web of paper is complete. In isolating the bast fibres employed in the textile industries, a preliminary partial disintegration of the plant stem is brought about by the process of steeping or retting, by which the separation of fibre from fleshy or cellular tissue is much facilitated.

Last in order of simplicity of distribution, we have the fibres known to the botanist as the fibro-vascular bundles of leaves and monocotyledonous stems, these bundles being irregularly distributed through the main cellular mass, and consequently, by reason of adhesion thereto, much more difficult of isolation. For this and other reasons, more or less in correlation with natural function, we shall find this class of raw material lowest in value to the paper-maker.

It is necessary at this stage to point out that the work of the paper-maker and that of the textile manufacturer are complementary one to the other, and the supply of fibrous raw material is correspondingly divided: it may be said, indeed, that the paper industry subsists largely upon the rejecta of the textile manufactures. The working up of discontinuous fibre elements into thread, which is the purpose of the complicated operations of the spinner, is conditioned by the length and strength of these ultimate fibres. Paper-making, on the other hand, requires that the raw material shall be previously reduced to the condition of minute subdivision of the constituent fibres, and therefore can avail itself of fibrous raw material altogether valueless to the spinner, and of textile materials which from any cause have become of no value as such. To the raw materials of the paper-maker, which we have briefly outlined above, we must therefore add, as a supplementary class, textiles of all kinds, such as rags, rope and thread.

During the latter part of this century, and in response to the enormously increased demands upon the sources of supply, there has come the exploitation of the fibrous woods for paper-making purposes.

Having thus acquired a general idea of the sources of our raw materials, we must study more closely the substances themselves; and, first of all, we must investigate them as we should any other chemical substance, i.e. we must get to understand the nature and properties of the matter of which the vegetable fibres are composed. While these exhibit certain variations, which are considerable, the substances present a sufficient chemical uniformity to warrant their being designated under a class name : this name is Cellulose. The prototype of the celluloses is the cotton fibre.

CHAPTER I.

CELLULOSE.

CELLULOSE is the predominating constituent of plant tissues, and may be shortly described as the structural basis of the vegetable world. Constituting, as it does, the material framework or skeleton of the plant, or plant cell, this more permanent function implies a corresponding resistance to the destructive agencies of the natural world: in other words, considered as a chemical individual, cellulose is extremely inert, or non-reactive. It is resistant to the hydrolysing action of alkalis and acids, to oxidants; and, as a 'saturated' carbon compound, has no tendency to combine directly with the halogen elements, e.g. chlorine and bromine. These main features of its negative chemical characteristics are mentioned thus early in explanation of the methods employed for its isolation in the laboratory. Cellulose never occurs in the plant in the free state, but always in admixture or combination with other groups: members of the fatty series ('fat and wax' constituents); the aromatic series (colouring matters, tannins); the pectic group of more or less oxidised, and therefore acid, derivatives of the carbohydrates. These latter yield to the attack of one or other of the reagents towards which cellulose is inert; and hence the following general method of removing these 'impurities' in the form of soluble derivatives, and of isolating the cellulose as the resistant residue: (*a*) the fibrous raw material is boiled with a dilute solution of sodium hydrate (1–2 p.ct. $NaOH$), and, after thorough washing, is (*b*) exposed in the moist state to an atmosphere of chlorine gas; (*c*) it is again treated with boiling alkaline solution. By such treatment of the majority of vegetable tissues, the 'non-cellulose' constituents are removed, and a residue of cellulose obtained. A slight treatment with a bleaching agent, to remove residues of coloured impurities, and a final washing with alcohol and ether, completes the purification, and the cellulose is obtained as a mass of 'ultimate fibres' of pure white colour, more or less translucent.

Though purified by the removal of 'non-cellulose' groups, such as above indicated, the residue of cellulose is not necessarily 'pure' in the sense understood by the chemist, that is, it cannot be taken to represent a single homogeneous substance.

On the contrary, we shall show that the paper-makers' 'celluloses'—obtained by a large variety of drastic treatments of fibrous raw materials—are mixtures of celluloses of different constitution.

Cotton cellulose, however, when fully purified, may be regarded as a chemically pure substance, and in setting forth the outline of the chemistry of cellulose, we shall at first confine ourselves to this typical representative of the group.

Empirical Composition.—Cellulose is a compound of carbon, hydrogen and oxygen, united in the percentage proportions—

C	44·2
H	6·3
O	49·5

corresponding with the statistical formula $C_6H_{10}O_5$, by which also it is defined as a 'carbohydrate.' The above numbers represent the composition of the 'ash-free' cellulose. All vegetable tissues contain inorganic or mineral constituents, of which a certain proportion is retained by the cellulose, isolated as described, or by any of the processes practised on the large scale in the arts. The celluloses burn with a quiet luminous flame, leaving these inorganic constituents as an ash. In bleached cotton the average proportion of ash is 0·1–0·4 p.ct.

In the preparation of filter paper for chemical use it is important to reduce this impurity to a minimum, which is effected by treatment with hydrofluoric and other acids. 'Swedish' filter paper contains 0·03–0·05 p.ct. ash constituents, representing about $\frac{1}{1000}$ mgr. per sq. cm. of area; and is the purest form of cellulose with which we can deal.

Cellulose and Water. Cellulose Hydrates.—All vegetable structures in the air-dry condition retain a certain proportion of water—or *hygroscopic moisture*, as it is termed—which is readily driven off on heating, but regained on exposure to the atmosphere under ordinary conditions. The mean percentage of this 'water of condition' varies from 6 to 12 in the several celluloses: in any given cellulose variations of 1–2 p.ct. from the mean number follow the variations in the hygrometric condition of the atmosphere. The factor of 'normal moisture' is of obvious importance in commercial dealings in celluloses. Thus, for the 'wood pulps' (celluloses), the 'standard moisture' commonly adopted is '10 p.ct.'—that is, 100 parts of the air-dry pulp yield on drying, at 100°, 90 parts dry cellulose. Conversely, in calculating from the basis of dry cellulose $= a$, to 'air-dry with 10 p.ct. moisture' $= b$, it is clear that $b = \frac{10}{9} a$. The proportion of water held by the celluloses in an atmosphere saturated with aqueous vapour is necessarily very much greater than in the ordinary atmosphere, partially saturated at the same temperature.* The celluloses or compound celluloses (*supra*) as they occur in the plant are characterised by a wide range of hydration phenomena. Plant tissues in the early stages of growth take the form of gelatinous hydrates, the proportion of water combining with the organic colloid in these hydrates being very large, e.g. 80 p.ct. of the weight of the hydrate. The re-hydration of the mature celluloses to these forms is determined by certain reagents as a stage in their conversion into the fully soluble form. Such processes of solution of cellulose we proceed to consider.

Solutions of Cellulose.—Cellulose is insoluble in water

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* See H. Müller, Pflanzenfaser. p. 3.

as in all simple solvents. In presence of certain metallic compounds, however, it combines with water, passing, as above described, through the conditions of gelatinous hydrates, and finally disappearing to form a homogeneous viscous solution. Of such solvents of cellulose the simplest is (1) zinc chloride in concentrated aqueous solution (40 p.ct. $ZnCl_2$). The solution process requires the aid of heat (60–100°), and may be carried out as follows: 4–6 parts $ZnCl_2$ are dissolved in 6–10 parts water, and 1 part cellulose (bleached cotton) stirred in till evenly moistened. The mixture is digested at first at 60–80°, when the cellulose is gelatinised; the solution is completed by exposure to water-bath heat, stirring from time to time, and replacing the water which evaporates. In this way a homogeneous syrup is obtained. The solution is entirely decomposed by dilution, the cellulose being precipitated as a hydrate in combination with zinc oxide. On washing with hydrochloric acid a pure cellulose hydrate is obtained, the quantity recovered being approximately equal to the original cellulose taken. When precipitated by alcohol, a compound of cellulose and zinc oxide is obtained with 18–25 p.ct. ZnO, i.e. in the approximate molecular ratio $2C_6H_{10}O_5ZnO$.

Technical Applications.—(*a*) The precipitation of the syrupy solution by alcohol is of such a character as to permit of a continuous production of thread or film, the solution being 'squirted' under pressure from a fine glass orifice into the alcohol. The thread, when purified, is carbonised in closed vessels, to form the very resistant carbon constituting the filament for incandescent electric lamps. (*b*) *Vulcanised fibre* is produced by treating a suitable paper (1 part) with a zinc chloride of 65–75° B (4 parts). When the constituent fibres are superficially gelatinised, the sheets are welded together under pressure into very compact masses. These are then purified, and subjected to further treatment to render them waterproof.*

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* German Patent 3181 (1878): C. Hofmann, Prakt. Handb. Papierf., p. 170.

(2) Zinc Chloride and Hydrochloric Acid.—If the $ZnCl_2$ is dissolved in twice its weight of aqueous hydrochloric acid (40 p.ct. HCl), a solution is obtained which dissolves cellulose rapidly in the cold. If quickly diluted the cellulose is recovered with but little change, but on standing it is resolved into products of lower molecular weight (dextrins, &c.) entirely soluble in water. The solution is a useful aid to investigations in the laboratory, but so far has received no industrial applications.

(3) Ammoniacal Cupric Oxide.—The solutions of the cuprammonium compounds generally, in presence of excess of ammonia, attack the celluloses rapidly in the cold, forming a series of gelatinous hydrates, passing ultimately into fully soluble forms. The solutions of the pure cuprammonium hydroxide are more active in producing these effects than the solutions resulting from the decomposition of a copper salt with excess of ammonia. Two methods are in common use for the preparation of these solutions, which should contain—

10–15 p.ct. ammonia (NH_3).
2·0–2·5 p.ct. copper (as CuO).

(1) Hydrated cupric oxide is prepared by precipitating a solution of cupric sulphate at 2 p.ct. strength with a slight excess of sodium hydrate, also in very dilute solution. The precipitate is washed till entirely free from alkali. The original solution in which the precipitation takes place, and the water used in washing, should contain a small portion of glycerin, 0·05 to 0·10 p.ct. The washed precipitate is fully drained, and then mixed with a quantity of a 10 p.ct. solution of glycerin—in contact with which it may be preserved unchanged in stoppered bottles. Prior to dissolving in 15–20 p.ct. NH_3 for use, the oxide may be washed free from glycerin, should the presence of the latter be objectionable.*

(2) Metallic copper in the form of sheet or turnings is placed in a cylinder and covered with strong ammonia; atmospheric air is caused to bubble through the column of liquid

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* Fassbender: Berl. Ber. 13, 1822.

at a rate calculated to forty times the volume of the liquid used per hour. In about six hours a liquid of the requisite composition is obtained.

Solutions of cellulose of 5–10 p.ct. (cellulose) strength, are readily prepared by digestion in the cold with 20–10 times its weight of the solution. The solutions are rather 'ropy' and gelatinous than viscous. The cellulose is readily precipitated from the solutions: (*a*) by neutral dehydrating agents, such as alcohol, sodium chloride and other salts of the alkalis; (*b*) by acids. In the latter case the cellulose is precipitated in the 'pure' state, i.e. free from cupric oxide. It retains a large proportion of water of hydration. On drying by heat, the gelatinous hydrate changes by molecular aggregation into compact horny masses.

Technical Applications.—This property of gelatinising and dissolving cellulose has been taken advantage of in important industrial applications of the cuprammonium compounds. Vegetable textile fabrics and paper, passed through a bath of the cuprammonium hydroxide, are 'surfaced' by the film of gelatinised cellulose, which retains the copper oxide (hydrate) in such a way that it dries to a bright malachite green colour, the ammonia of course escaping. By this treatment the fibres are further compacted together, and the fabric acquires a water-resistant character; the presence of the copper oxide is also preservative against the attacks of mildew, insects, &c. If the fabrics are rolled or pressed together when in the gelatinised condition, they become welded together on drying, and a variety of compound textures are produced in this way. The fabrics are sold in this country under the style of 'Willesden' goods. Recently, also, the solution has been applied to the production of an artificial thread of high lustre, a so-called 'artificial silk.'

Cellulose and Hydrolytic Agents.—Without attempting a theory, or even an explanation, of the action of the solvents we have just described, there is one aspect which claims attention, and will be more clearly grasped from what follows in the present section: that is, that the cellulose molecule contains OH groups of opposite function, giving it some of the characteristics of the inorganic salts; that it yields to the action of zinc chloride by reciprocal interaction of its OH groups with those of the salt in solution, and that the dissolution of the cellulose is therefore due to a species of double salt formation.

An incipient activity of this kind is manifested by cellulose in contact with highly dilute solutions of alkalis and acids, the active reagent being absorbed by the cellulose in perceptible degree. The amount though small is definite, and sufficient to allow of the establishment of a definite *ratio* of absorption from equivalent solutions of alkalis and acids. Thus, with typical members of the two groups, the molecular ratio of absorption is 10 NaOH : 3 HCl.* The phenomenon has been more recently studied from the independent standpoint of thermal equilibrium. It has been shown that when pure cotton is plunged into dilute solutions of the acids and alkalis, liberation of heat takes place. The rise of temperature was found to be slow, and, under the conditions chosen for the experiments, ceases after the lapse of seven to eight minutes.

The following are typical results in calories per 100 grms. of cotton:—

—	KOH.	NaOH.	HCl.	H_2SO_4.
Raw cotton	1·30	1·08	0·65	0·60
Bleached	2·27	2·20	0·65	0·58

L. Vignon.

It would appear from these results that cellulose has the properties of a feeble acid, and of a yet feebler base. From the comparative insignificance of the 'affinities' involved, it might be inferred that they may be neglected in practical and industrial operations. So far from this being the case

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* Mills.

it must be remembered that the combination of cellulose with colouring matters, i.e. the dyeing properties of the fibre substance, are largely dependent upon a play of affinities of this particular order. So also the auxiliary processes of mordanting, in which the fibre absorbs both acids and basic oxides from dilute saline solutions; these oxides, in combination with the fibre substance, enabling it in turn to take up particular colouring matters from their solutions. Formerly it was much discussed as to whether dyeing phenomena were of the 'physical' or 'chemical' order. The modern view does not concern itself so much with definitions as to insist that the phenomena are molecular. This chemical aspect is prominent in the reciprocal play of acid and basic functions of the constituent groups of both fibre-substance and colouring matter (and mordant); the 'physical' side is brought into evidence by certain properties of the fibres which are bound up with their minute structure, and which evidently play an important part in the absorption of reagents from solution, viz. the phenomena of *capillary transmission* of liquids. Schönbein appears to have been the first to observe that strips of unsized paper of which one end is placed in an aqueous solution, e.g of a metallic salt, will absorb and transmit the water more rapidly than the dissolved salt, which is therefore 'filtered out'; further, that to the various salts cellulose manifests varying degrees of resistance to transmission in solution. These phenomena have been further studied by Lloyd,* for metallic salts, more recently by E. Fischer and Schmidmer,† and by F. Goppelsroeder for various colouring matters;‡ the results of their observations constituting the beginnings of a method of capillary analysis or separation. Without further discussing the phenomena from a theoretical standpoint, we may point out that they are of direct practical moment to the paper-maker: since, first, they have to be reckoned with in every one of his manufacturing operations; secondly, in one of the most important

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* Chem. News, 51, 81. † Liebig Ann., 272, 156.
‡ Berl. Ber., 20, 604.

applications of paper, viz. for writing purposes, the penetration of the paper by the ink, its indelible fixation, and the kind of press copy obtainable, are points largely affected or determined by such inter-actions as we have been considering.

It will be remembered that we have followed up the various matters dealt with in this section from the initial observation of the behaviour of cellulose to typical hydrolytic agents in cold dilute solution. These are absorbed, as we have seen, to form what we may term contact compounds, and they are an index of the hydrolytic changes which are determined by these compounds acting in more concentrated forms and at higher temperatures. *Hydrolysis* is essentially a process of resolution or decomposition: it is the loosening or undoing of a bond of union through combination with the elements of water. The agent which determines the change is the hydrolytic agent: and of such agents the most important are the (*a*) acids and (*b*) alkalis on the one hand, and (*c*) on the other, a class of carbon compounds known as soluble or unorganised ferments, or by the more modern term Enzymes. Cellulose yields to hydrolysis of both types.

(*a*) ACIDS.—The mineral acids of concentration equal to semi-normal at the boiling temperature, rapidly disintegrate the fibrous celluloses, as a consequence of molecular changes in the fibre-substance. The modified cellulose is brittle and pulverulent. Its composition is changed to that of a *hydrate* of the formula $2 \cdot C_6H_{10}O_5 \,.\, H_2O$, and it is therefore termed hydro- or hydra-cellulose, the chemical properties of which are described in a later section. The time required for completing this change varies with the temperature and concentration of the acid. The acid treatments of cellulose textiles which are necessary incidents of bleaching and dyeing operations are carried out well within the limits of safety—for the most part in the cold ($<20°$ C.) and with acids of less than 2 p.ct. strength (HCl, H_2SO_4). In dyeing operations requiring an acid bath and the boiling temperature, 'free' mineral acids are as much as possible avoided, acetic acid being substituted—an acid of low hydrolysing activity, and without sensible action on cotton. Paper is usually finished from the machine with a slightly acid *reaction*, but the utmost care is required to ensure the absence of 'free' acid.

(*b*) ALKALIS.—To alkaline solutions of equivalent strength, e.g. solutions of caustic soda of 1–2 p.ct. Na_2O, cotton cellulose is extremely resistant, even at temperatures exceeding 100.° The principal operations in the process of bleaching cotton and linen textiles consist in drastic alkaline treatments of this kind, whereby the non-cellulose constituents of the fibres are hydrolysed to products soluble in the alkaline lye. The oxidation processes which follow, e.g. treatment with the hypochlorites, permanganates, &c., in dilute solutions, although they may be regarded as the bleaching processes proper, really accomplish very little beyond removing residues or by-products of the alkaline treatment. It is also evident that resistance to alkaline treatment such as soaping, is a very important condition of the everyday uses of cellulose textiles.

At higher concentration and temperature the typical cellulose is attacked by the alkaline hydrates and converted into soluble derivatives. Thus, purified cotton cellulose digested three times in succession with solutions of 3 p.ct. Na_2O, was found to lose * :—

at 1 atm. pressure	12·1 p.ct.
5 "	15·4 "
10 "	20·3 "

With solutions of 8 p.ct. Na_2O under similar conditions the losses were 22·0, 28·0 and 59·0 p.ct. The processes of isolating paper-makers' celluloses largely consist in severe alkaline treatments, the conditions of which require adjustment to secure the most complete removal of the non-cellulose constituents of the raw materials, with the minimum of action (hydrolysis) on the cellulose.

A process of estimating cellulose in fibrous raw materials in the laboratory, based upon the action of alkaline hydrates

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* H. Tauss, Journ. Soc. Chem. Ind. 1889, 913; 1890, 883.

at elevated temperatures (150–180°), has been proposed by Lange.* The process rests upon the assumption that the celluloses are not attacked under the severe conditions of alkaline treatment adopted. This assumption cannot be maintained in view of the results above cited; the process has, moreover, been subjected to a careful critical investigation by Tollens,† who finds that it is subject to large and variable errors.

(*c*) ENZYMES.—A typical case of enzyme action is that of the conversion of the starches of cereals into fermentable sugars, in the operations (1) of malting the grain, (2) of 'mashing' the malt with water, to the solution or wort in which the sugars formed from the starch are in a condition to yield readily to the attack of the yeast-cell, undergoing further hydrolysis under the action of the yeast enzyme, and being finally broken down to alcohol and carbonic acid. The starches resemble the typical celluloses in the following particulars: they have the same empirical formula $n[C_6 H_{10}O_5]$; they are poly-anhydrides of hexose molecules, each hexose molecule losing water in the proportion of one molecule —thus m. $2C_6H_{12}O_6 -$ m. $2H_2O$—in *condensing* to form the anhydride; the highly complex molecule of the latter takes up water under the influence of hydrolytic treatments—in sucessive stages, *but special to each*—giving a similarly complex series of intermediate (i.e. partially hydrated) molecules, these breaking up finally (i.e. by complete hydration) to the typical hexose, dextrose.

Starch, under the influence of the enzyme of malt, termed *diastase*, yields the series of dextrins, amylins, malto-dextrins, maltose, and finally dextrose. To convey some idea of the complications presented by the series, it may be noted that it is necessary to expand the original starch molecule to $5[C_{12}H_{20}O_{10}]_{20}$. The first effect of hydrolysis is to split this into a resistant *dextrin* of the formula $[C_{12}H_{20}O_{10}]_{20}$, and a group of amylins representing the remaining four-

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* Ztschr. Physiol. Chem., 14.

† Suringar and Tollens, Ztschr. Angew. Chem. 1896, No. 23.

fifths of the molecule which pass through further hydration stages represented by such formulæ as $[C_{12}H_{20}O_{10}]n + H_2O$, maltose groups being successively formed and split off. Yeast, again, secretes an enzyme termed *invertase*, which hydrates the crystallisable but still complex sugars such as maltose and cane sugar [both $C_{12}H_{22}O_{11}$] to the simple hexose $C_6H_{12}O_6$.

No enzyme has yet been discovered which enables us to carry out a similar 'conversion' or hydration of cellulose in the laboratory. That such actions take place in plant life has been abundantly established. (*a*) In the germination of seeds the cell-walls (cellulose) are broken down to supply nutriment to the embryo. (*b*) In the attack of parasitic plants, dense structures of the 'host' are penetrated by the most delicate hyphæ of the invading organism by a dissolution and resolution of the original cellulose structure. (*c*) Brown and Morris have succeeded in cultivating the excised embryos of the cereals on artificial endosperms, and in showing that a cytohydrolytic enzyme is secreted which is sufficiently powerful in its action as to attack (i.e. hydrolyse) the typical cotton cellulose.

While, therefore, we may expect in the future to be furnished with the means of studying an enzyme hydrolysis or dissection of cellulose, we are at present limited to the action of powerful reagents such as the concentrated mineral acids, which, in a later section, we shall show to resolve cellulose through a series of hydration products (amyloid, dextrins, dextrose) presenting many analogies with the starch-dextrose series above described.

Cellulose, therefore, while an analogue of starch, is differentiated from it by an enormously greater resistance to hydrolytic actions of all kinds, which must express a corresponding difference in constitution.

We have now to study the actions of hydrolytic agents in *their more concentrated forms.*

(*a*) **Alkalis.**—Cold solutions of the alkaline hydrates of a certain concentration exert a remarkable effect upon the celluloses. Solution of sodium hydrate, at strengths exceeding 10 p.ct. Na_2O, when brought into contact with the cotton fibre at the ordinary temperature, instantly changes its structural features, i.e. from a flattened riband with a large central canal, produces a thickened cylinder with the canal more or less obliterated. These effects in the mass, e.g. in cotton cloth, are seen in a considerable shrinkage of length and width, with corresponding thickening, the fabric becoming translucent at the same time. The results are due to a definite reaction between the cellulose and the alkaline hydrates, in the molecular ratio $C_{12}H_{20}O_{10}$: 2NaOH, accompanied by combination with water (hydration). The compound of the cellulose and alkali which is formed is decomposed on washing with water, the alkali being recovered unchanged, the cellulose reappearing in a modified form, viz. as the hydrate $(C_{12}H_{20}O_{10}.H_2O)$. By treatment with alcohol, on the other hand, one half of the alkali is removed in solution, the reacting groups remaining associated in the ratio $C_{12}H_{20}O_{10}$: NaOH. The reaction is known as that of Mercerisation, after the name of Mercer, by whom it was discovered and exhaustively investigated.

Technical Applications.—Until quite recently, the observations of Mercer remained undeveloped. They are now applied on a large and increasing scale to the production of a silky lustre in cotton textiles. It is found that if during the action of the alkaline lye the cotton goods are kept under strain, the physical changes determined in the fibres enable it to produce that concentrated reflection of incident light which causes lustre.* These structural changes are permanent, persisting after the removal of the alkali by washing.

ALKALI CELLULOSE.—The compounds resulting from the union of cellulose and the alkaline hydrates, though of little stability—as we have seen—are still well-defined products. This fact is emphasised by the production from the alkali cellulose of two series of characteristic derivatives of cellu-

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* Rev. Gen. d. Mat. Col. 1898.

lose: (*a*) the sulpho-carbonates; (*b*) the benzoates—which are described in later sections.

(*β*) The **Acids** in concentrated form act in two opposite directions upon cellulose: (1) they attack and resolve the cellulose complex by processes of condensation and hydrolysis; (2) they *combine* with the cellulose (OH groups) to form acid ethers or *esters*. The consideration of the latter we defer until we have completed our survey of hydrolytic actions by now describing briefly those determined by the mineral acids in their more concentrated forms.

HYDROCHLORIC ACID in presence of water rapidly converts the fibrous cotton cellulose into a friable substance, the formation of which is not attended by any visible changes; but, on subjecting the product to pressure or mechanical action, it becomes a more or less structureless powder.

This product, known as hydro- or hydra cellulose, was first investigated as a cellulose derivative by A. Girard;* but the physical changes of the cotton fibre under the actions of acids which accompany the formation of this product had previously been studied by various observers.

SULPHURIC ACID.—Hydro-cellulose results also from the action, at ordinary temperatures, of sulphuric acid at certain dilutions. The following points have been established by C. Koechlin.† What may be called the critical concentration of the acid in regard to the production of hydro-cellulose lies between the limits 60–80° B. Thus, with the mixture of 3 vols. of the concentrated acid and 8 vols. water—i.e. an acid of 69° B—at the ordinary temperature, its action upon cotton does not become evident till after three hours' exposure. With an aqueous acid containing 100 grams H_2SO_4 per litre and at 80° C., the first appearances of change in the cotton are noted at the expiration of five minutes; after thirty minutes' exposure there is sensible disintegration; after sixty minutes the conversion is complete, i.e. into a friable mass of hydro-cellulose.

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* Mémoire sur l'Hydrocelluloses. Paris, 1881. Gauthier-Villers.

† Bull. Mulhouse, 1888.

The subjoined are analyses of specimens produced under very variable conditions of treatment of the cotton :—

—	(1)	(2)	(3)	(4)	$C_{12}H_{22}O_{11}$
Carbon . . .	42·10	42·50	42·04	41·80	42·1
Hydrogen . .	6·30	6·50	6·70	6·70	6·4
Oxygen . . .	51·60	51·00	51·26	51·50	51·5

Viz. (1) and (2) by the action of sulphuric acid of 45° B.; (3) by the action of gaseous hydrochloric acid in presence of moisture; (4) by the action of dilute sulphuric acid (3 p.ct. H_2SO_4) at 60° C. The action of such acids, therefore, which do not combine with the cellulose to form definite *esters* (*infra*) is one of hydration and hydrolysis, the insoluble product tending to a limit represented by the formula $n[C_{12}H_{20}O_{10}.H_2O]$. The hydration of cellulose to such a product is attended by a gain of weight. But the reaction studied in the mass, i.e. as an aggregate effect, is always attended by *loss* of weight, the hydro-cellulose weighing less, and under some conditions of action of acids, much less than the original cellulose. This is due to a further hydrolysis of a portion of the cellulose to products soluble in water—tending, in fact, to the limit of extreme hydrolysis to dextrose. The reaction, in fact, is a complicated one, condensation or dehydration playing an important part in the changes which may, in the net or aggregate effect, result in a hydration of the cellulose.

The properties of the hydro-cellulose are in some respects those of cellulose: it dissolves, though more readily, in the special solvents of cellulose; and combines, but also more readily, with nitric acid (*infra*) to form a similar series of nitrates. Generally it is in all respects much more reactive.

It rapidly oxidises when heated at 100°, with discoloration; the brown-coloured products of oxidation are soluble in water, and reduce Fehling's solution. Hydro-cellulose is attacked by dilute alkalis and dissolved more or less; the solutions are yellow in colour and reduce Fehling's solution.

It is clear, therefore, that the main characteristics of the hydro-cellulose series is a progressive *hydrolysis* of the cellulose, with liberation of the CO groups of the constituent hexose units. These hydrolytic changes are attended by progressive structural disintegration, and the products have lost the characteristics of chemical inactivity. In all properties, therefore, which determine the industrial value of cellulose, and notably to the paper-maker, the hydro-celluloses are inferior, or degradation products.

Technical Applications.—The removal of vegetable fibres from mixed woollen refuse (shoddy), and of vegetable impurities from raw wool, is effected by acid treatments of various degrees such as we have described, and to which the wool is resistant. To the paper-maker hydro-cellulose has first the negative importance that he has by all means to avoid its production in the finished web or sheet.

SULPHURIC ACID.—Di- and tri-hydrate—$H_2SO_4.2H_2O$, $H_2SO_4.3H_2O$—produce a special series of hydration effects. Unsized paper plunged into sulphuric acid diluted previously with $\frac{1}{3}$ to $\frac{1}{4}$ its volume of water and cooled, is rapidly attacked, the paper becoming transparent, owing to the swelling and gelatinisation of the fibres. The reaction quickly becomes one of solution; but if the paper be transferred after short exposure to water, the acid compound is decomposed, and the resulting gelatinous hydrate is precipitated *in situ*. The product, after exhaustive washing and drying, is obtained as *parchment paper*. This modification gives a tough translucent sheet.

The hydrated compound itself, produced as described, from its resemblance to starch, has been termed *amyloid*. Its empirical composition is that of the hydro-celluloses, viz. $n\ [C_{12}H_{22}O_{11}]$, to which compounds also it is closely allied in chemical properties.*

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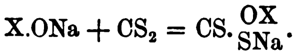
* See 'Soluble and Insoluble Colloidal Cellulose and Composition of Parchment Paper.' Guignet. Compt. Rend., 108, 1258.

Technical Application.—The process as described above is carried out industrially on 'continuous' machinery, the parchment paper being produced in endless length. The product is variously applied as a substitute for paper where resistance to water is required.

Nitric Acid of sp. gr. 1·4 also produces (without oxidation) an effect of a similar character. A short immersion of unsized paper, e.g. filter paper, in the acid, followed by copious washing, has a considerable toughening action, attended by a shinkage in linear dimensions of about $\frac{1}{10}$.* The effect is made use of in the laboratory as a convenient method of toughening filter papers when required to stand exceptional fluid pressures.

To follow a strictly logical order of treatment, we should describe here the compounds of cellulose, with *acid radicals* — the *cellulose esters*: for instance, the sulphates and nitrates which are formed on bringing cellulose in contact with the respective concentrated acids. But we defer the mention of these to a later section, for the reasons (1) that they have only an indirect bearing on the technology of papermaking, and (2) that we have yet to continue the discussion of the relationship of cellulose to *water* and *oxygen*, upon the basis of the views which have been gradually developed to this point.

Sulpho-Carbonates of Cellulose [Cellulose xanthogenic acid].—We have shown that cellulose combines with the alkaline hydrates, and when the resulting compound, or alkali-cellulose (hydrate), is exposed to the action of carbon disulphide at the ordinary temperature, a simple synthesis takes place, which may be formulated by the typical equation:



$$X.ONa + CS_2 = CS.\genfrac{}{}{0pt}{}{OX}{SNa}.$$

The best conditions for the reaction appear to be when the reagents are brought together in the molecular proportions:

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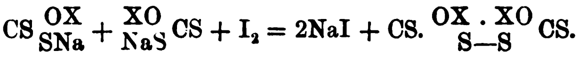
* See Journ. Chem. Soc., 47, 183.

$$\underset{162}{C_6H_{10}O_5} \quad \underset{2\times 40}{2NaOH} \quad \underset{76}{CS_2} \quad [30\text{–}40H_2O];$$

the second ONa group being in direct union with the cellulose molecule, which reacts, therefore, as an alkali cellulose. The resulting compound may therefore be described as an alkali-cellulose-xanthate. It is perfectly soluble in water, to a solution of extraordinary viscosity. The course of the reaction by which it is produced is marked by the further swelling of the mercerised fibre and a gradual conversion into a gelatinous transparent mass, which dissolves to a homogeneous solution on treatment with water.

To carry out the reaction in practice, bleached cotton is treated with excess of a 15 p.ct. solution of NaOH, and squeezed till it retains about three times its weight of the solution. It is then placed in a stoppered bottle with carbon disulphide, the quantity being about 50 p.ct. of the weight of the cotton. After standing about three hours at ordinary temperatures, water is added sufficient to cover the mass, and the further hydration of the compound allowed to proceed spontaneously some hours (e.g. over night). On stirring, a homogeneous liquid is obtained, which may be diluted to any required degree.

Thus prepared, the crude solution is of a yellow colour, due to by-products of the reaction (trithiocarbonates). The pure compound is obtained either by treatment of the solution with saturated brine or with alcohol. It forms a greenish-white flocculent mass or coagulum, which redissolves in water to a colourless or faintly yellow coloured solution. Solutions of the salts of the heavy metals added to this solution precipitate the corresponding xanthates. Iodine acts according to the typical equation:



$$CS\begin{matrix}OX\\SNa\end{matrix} + \begin{matrix}XO\\NaS\end{matrix}CS + I_2 = 2NaI + CS.\begin{matrix}OX\;.\;XO\\S\text{—}S\end{matrix}CS.$$

The compound, which may be described as a cellulose dioxythiocarbonate, is precipitated in the flocculent form; it is redissolved by alkaline solution, in presence of reducing agents, to form the original compound.

The most characteristic property of the cellulose xanthates is (*a*) their *spontaneous decomposition* into cellulose (hydrate), alkali, and carbon disulphide—or products of interaction of the latter. When this decomposition proceeds in aqueous solution, at any degree of concentration exceeding 1 p.ct. cellulose, a jelly or coagulum is produced, of the volume of the containing vessel. These highly hydrated modifications of cellulose lose water very gradually, the shrinkage of the 'solid' taking place symmetrically. The following observations upon a 5 p.ct. solution (cellulose), kept at the ordinary atmospheric temperature, will convey a general idea of the phenomena attending the regeneration of cellulose from the alkali xanthate. The observations were made upon the solution kept in a stoppered cylinder; after coagulation, the solution, expressed from the coagulum of cellulose by spontaneous shrinkage, was removed at intervals. Original volume of solution, 100 c.c.

	Time in days.	Vol. of cellulose hydrate. c.c.	Diff. from 100 c.c. = vol. expressed. c.c.
Coagulation	8th day		
First appearance of liquid	11th "		
	16th "	98·0	2·0
	20th "	83·5	16·5
	25th "	72·0	28·0
	30th "	58·0	42·0
	40th "	42·8	57·2
	47th "	38·5	61·5

The shrinkage from a 5 p.ct. to a 10 p.ct. coagulum of cellulose hydrate is therefore extremely slow and fairly regular; from 10–12 p.ct. there is considerable retardation; and at 12–15 p.ct. the coagulum may be considered as a hydrate, stable in a moist atmosphere. It follows from these observations that if a 10–12 p.ct. solution be allowed to coagulate spontaneously, the resulting cellulose hydrate will undergo very small shrinkage if kept in a moist atmosphere. These observations indicate the uses which can be made of the solution in preparing cellulose casts and moulds.

As regards the problem of hydration and dehydration of the cellulose there are, of course, other methods of approximately determining the 'force' by which the water molecules are held. It is a problem of wide significance, by reason of the important part played by such hydrates in the economy of plant life. Further investigations of the problem, therefore, by the various known methods are being prosecuted.

(*b*) *Coagulation by heat.*—The solution may be evaporated at low temperatures to a dry solid, perfectly re-soluble in water. If heated at 70–80°, however, the solution thickens; and at 80–90° the coagulation (i.e. decomposition) is rapidly completed. If the solution be dried down at this temperature in thin films, it adheres with great tenacity to the surface upon which it is dried. On treatment with water, however, the cellulose film may be detached, and when freed from the by-products of the reaction the cellulose is obtained as a homogeneous transparent colourless sheet or film, of great toughness, which, on drying, hardens somewhat, increasing in toughness and preserving a considerable degree of elasticity. From the properties of the solution and of the cellulose regenerated from it, it will be seen that both are capable of extensive applications.

QUANTITATIVE REGENERATION OF CELLULOSE FROM SOLUTION AS THIOCARBONATE.—Very careful experiments have been made to determine the proportion of cellulose recovered from solution as thiocarbonate. Weighed quantities of Swedish filter paper were dissolved by the process, and the solutions treated as follows: (*a*) allowed to 'solidify' spontaneously at 15–18°; (*b*) coagulated more rapidly at 55–65°; (*c*) sulphurous acid was added in quantity sufficient to combine with one-third of the alkali present in the solution—the resulting solution being colourless: this was then set aside to coagulate spontaneously. The regenerated celluloses were exhaustively purified, by boiling in sodium sulphite solution, digesting in acid, digesting in water, &c., and, repeating the treatments until pure, they were finally dried at 60° and finished at 100°.

The following results were obtained :—

	Weight of original cellulose.	Weight of regenerated cellulose.
(*a*)	1·7335	1·7480
(*b*)	1·7415	1·7560
(*c*)	1·8030	1·8350

The results show a net difference of 1·1 p.ct. (increase), a quantity which, for practical purposes, may be neglected. As, however, the empirical composition of the regenerated cellulose indicates hydration to $4C_6H_{10}O_5.H_2O$ (*infra*), and a corresponding gain of 2·7 p.ct., it appears that there is a slight hydrolysis of even this very pure form of cellulose to soluble products. From subsequent observations (p. 38) it will appear that the hydrolysis falls upon an oxycellulose, probably present in all bleached celluloses.

The *cellulose regenerated* from the thiocarbonate differs from the original cellulose, so far as has been ascertained, in the following respects :—

(1) Its *hygroscopic moisture*, or water of condition, is some 3–4 p.ct. higher, viz. from 9–10·5 p.ct.

(2) *Empirical composition.*—The mean results of analysis show $C = 43 \cdot 3$, $H = 6 \cdot 4$ p.ct., which are expressed by the empirical formula, $4C_6H_{10}O_5 \cdot H_2O$.

(3) *General properties*, in the main, are identical with those of the original, but the OH groups of this cellulose are in a more reactive condition. Thus, this form of cellulose is acetylated by merely heating with acetic anhydride at its boiling point, whereas normal cellulose requires a temperature of 180° C. (*Vide* Cellulose Acetates.)

As regards reaction in aqueous solution, we may notice that it has a superior dyeing capacity, and also combines with the soluble bases to a greater extent : e.g. if left some time in contact with a normal solution of sodium hydrate, it absorbs from 4·5–5·5 p.ct. of its weight in combination.

Towards the special solvents previously described it behaves similarly to the normal or fibrous cellulose; the solutions obtained are, however, more viscous and less gelatinous.

The thiocarbonate reaction throws light on that somewhat vague quantity, the 'reacting unit' of cellulose. We use this term in preference to that of molecular weight; for the latter quantity can be determined only for bodies which readily assume the simplest of states, and which can be ascertained by physical measurements to be in that state; whereas in the case of cellulose the ordinary criteria of molecular simplicity are quite inapplicable.

We have formulated the synthesis of the thiocarbonate as taking place by the interaction of $C_6H_{10}O_5 : 2NaOH : CS_2$; or in approximate percentage ratio—

Cellulose: Alkali: Carbon disulphide = 100 : 50 : 50;

or, again, in terms of the constituents estimated in the analysis of the product—

Cellulose: Alkali (Na_2O): Sulphur = 100 : 40 : 40.

If, now, the crude product be precipitated from aqueous solution by alcohol or brine, and again dissolved and reprecipitated, the ratio changes to 100 : 20 : 20; and, through a succession of similar treatments, the ratio of alkali and sulphur to cellulose continually diminishes the product, however, preserving its solubility. In fact, no definite break has been observed in the continuous passage from the compound as originally synthesised to the regenerated cellulose (hydrate). It is clear, therefore, that the reacting cellulose unit is a continually aggregating molecule; and if in the original synthesis it appears to react as $C_6H_{10}O_5$, so in a thiocarbonate containing, e.g. only 4 p.ct. Na_2O, the unit is $10C_6H_{10}O_5$. There being, moreover, no ascertainable break in the series, we have no data for assigning any limiting value to the reacting unit under these conditions. All we can say is, that the evidence we have points to its being of indefinite magnitude; and we can see no *a priori* reason why it should not be so.

In discussing this reaction we have left out of consideration the part played by the water. It may be noted that a

1 p.ct. solution of cellulose (as thiocarbonate) will 'set' to a firm jelly of hydrate, of the volume of the containing vessel; and that even at 0·25 p.ct. cellulose, gelatinisation of the liquid occurs in decomposition. We have also pointed out that a hydrate containing only 10 p ct. cellulose is a substantial solid which gives up water with extreme slowness.

Cellulose, therefore, affords conspicuous illustrations of the property which the 'colloids' have, as a class, of 'fixing' water, and of the modes in which this property takes effect. In regard to the causes underlying this peculiar relationship to water, we know as yet but little. It is to be noted that the group of colloids comprises bodies of very various chemical function, acids, bases, salts and compounds of mixed function, as in the complex carbohydrates and proteids; the only possible feature common to so varied a group would be that of molecular arrangement, favouring the aggregation of the molecules, together with those of water, to groups of indefinite magnitude. On this subject, however, conjectures must, for the present, do duty for a theory which can only be shaped by further investigation.

Technical applications.—The solutions of cellulose in the form of sulphocarbonate are prepared for industrial use at concentrations of 10–20 p.ct. (cellulose) according to requirement. The product in this form is known as 'viscose.' Its uses depend upon the ease with which the cellulose can be regenerated from the solution and in any desired form, viz. compact solid ('viscoid'), sheet or film, powder, or lastly thread ('lustra-cellulose')—retaining in these forms the essential properties of the original fibrous cellulose.

Viscose is used in the engine sizing of pulps for working up into paper and boards; in the coating of papers as the vehicle, chiefly for white pigments such as barium sulphate and China clay; in the preparation of filmed fabrics such as 'leather cloths;' and for a number of other similar purposes.

These applications all depend upon the relatively low cost of production of this particular solution of cellulose, together with the obvious advantages of an aqueous solution from which cellulose is directly regenerated by a variety of simple methods.

Cellulose and Acid Radicals: Cellulose Esters.—For the reasons previously given, these compounds will only be briefly described, i.e. only so far as is necessary to complete our review of the general chemistry of cellulose. While these derivatives are many of them of enormous industrial importance, they have only an indirect connection with the work of the paper-maker, and for further information we must refer him to special treatises.

An ester may be generally defined as a species of salt formed by union of an alcoholic OH group with an acid, water being formed and eliminated. In these reactions cellulose may be represented by its unit group $C_6H_{10}O_5$. In this unit there are several OH groups, each capable of such combination. On general grounds, in fact, it might be expected that four of the five atoms of O represent OH groups, and the formation of a *tetracetate* has supplied the proof that the formula may be written $C_6H_6O\,(OH)_4$. The highest nitrate which has been obtained is, on the other hand, the *tri-nitrate*, $C_6H_7O_2\,(ONO_2)_3$.

Certain of these esters may be formed without destroying the fibrous form of the original cellulose (nitrates, benzoates); in others the combination is attended by solution of the cellulose (acetates, sulphates). Similarly, from the amorphous modifications of cellulose, nitrates and benzoates may be formed without solution of the product.

Nitric Esters: Cellulose Nitrates.—These are the best known of the synthetical derivatives of cellulose, their discovery dating back over fifty years, during which period they have come into ever-increasing industrial application. They are formed by the inter-action of cellulose, in any form, and concentrated nitric acid. Water being formed simultaneously, it is usual to carry out the reaction in presence of sulphuric acid, which combines with and removes the water from the sphere of reaction.

A concise view of the entire series of these nitrates is given by Vieille in a paper entitled 'Sur les dégrès de la Nitrification limites de la Cellulose.'* From the title of this author's communication, it may be concluded that it is a study of the nitrations of cellulose (cotton) under the condition of progressive variations, with the view of determining the maximum fixation of the nitric group corresponding to such variations. The most important factor of the process is the concentration of the nitric acid, which was the variant investigated. The temperature was kept constant—11° C.—and the nitrating acid (nitric acid only) was employed in very large excess (100–150 times the weight of cellulose), so as to avoid disturbance of the results by rise of temperature or by dilution of the acid. The products were analysed by Schlœsing's method, and the analyses are expressed in c.c. NO (gas) (at 0° and 760 mm.) per 1 grm. of substance.

In regard to the time factor, or duration of exposure to the acid required to give the maximum number, this was in cases controlled by observation. Thus with the acid HNO_3, $\frac{1}{2}H_2O$ (1·488 sp. gr.), after 48 hours the product was still blued by iodine, and gave 161 c.c. NO; whereas after 62 hours' exposure the iodine reaction was not obtainable, and the maximum number (165·7 c.c. NO) was obtained. At the slightly lower gravity 1·483, an exposure of 120 hours was necessary. At the still lower gravity when the cotton (nitrate) passes into solution, the maximum is very rapidly attained (5 minutes).

The highest nitrate obtained as above, with nitric acid only, is somewhat lower than when sulphuric acid is present. Under these latter conditions the author regards the highest nitrate obtainable as $C_{24}H_{18}(NO_3H)_{11}O_9$.

The following is a brief account of the usual methods of preparation, and of the properties of the various products. In the case of this series the cellulose unit group is taken as $C_{12}H_{20}O_{10}$, by which device a nomenclature in fractional proportions is avoided.

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* Compt. Rend. 95 132.

Sp. gr. of acid.	Composition (approximate).	Analysis of Product c.c. NO per 1 grm.	Properties of Products.
1·502 1·497	$NO_3H.\frac{1}{4}H_2O$	202·1 197·9	Structural features of cotton preserved; soluble in acetic ether; *not* in ether-alcohol $C_{24}H_{20}(NO_3H)_{10}O_{10}$
1·496 1·492 1·490	$NO_3H.\frac{1}{3}H_2O$	194·4 187·3 183·7	Appearances unchanged; soluble in ether-alcohol; collodion cotton $C_{24}H_{22}(NO_3H)_9O_{11}$ $C_{24}H_{24}(NO_3H)_8O_{12}$
1·488 1·483	$NO_3H.\frac{1}{2}H_2O$	165·7 164·6	Fibre still unresolved; soluble as above, but solutions more gelatinous and thready $C_{24}H_{26}(NO_3H)_7O_{13}$
1·476 1·472 1·469	$NO_3H.\frac{3}{4}H_2O$	140·5 140·0 139·7	Dissolve cotton to viscous solution; products precipitated by water; gelatinised by acetic ether; *not* ether-alcohol $C_{24}H_{28}(NO_3H)_6O_{11}$
1·463 1·460 1·455 1·450	$NO_3H.H_2O$	128·6 122·7 115·9 108·9	Friable pulp; blued strongly by iodine in KI solution; insoluble in alcoholic solvents $C_{24}H_{30}.(NO_3H)_5O_{15}$ $C_{24}H_{32}(NO_3H)_4O_{16}$

Several well characterised nitrates have been formed, but it is a very difficult matter to prepare any one in a state of purity, and without admixture of a higher or lower nitrated body.

The following are known:—

Hexa-nitrate, $C_{12}H_{14}O_4(NO_3)_6$, gun-cotton. In the formation of this body, nitric acid of sp. gr. 1·5, and sulphuric acid of sp. gr. 1·84 are mixed, in varying proportions—about 3 of nitric to 1 of sulphuric. Sometimes this proportion is reversed, and cotton immersed in this at a temperature not exceeding 10° C. for 24 hours: 100 parts of cellulose yield about 175 of cellulose nitrate. The hexa-nitrate so prepared is insoluble in alcohol, ether, or mixtures of both, in glacial acetic acid or methyl alcohol. Acetone dissolves it very slowly. This is the most explosive gun-cotton. It ignites at 160°–

170° C. According to Eder, the mixtures of nitre and sulphuric acid do not give this nitrate. Ordinary gun-cotton may contain as much as 12 per cent. of nitrates soluble in ether-alcohol. The hexa-nitrate seems to be the only one quite insoluble in ether-alcohol.

Penta-nitrate, $C_{12}H_{15}O_5\ (NO_3)_5$. This composition has been very commonly ascribed to gun-cotton. It is difficult, if not impossible, to prepare it in a state of purity by the direct action of the acid on cellulose. The best method is the one devised by Eder, making use of the property discovered by de Vrij, that gun-cotton (hexa-nitrate) dissolves in nitric acid at about 80 or 90° C., and is precipitated, as the penta-nitrate, by sulphuric acid after cooling to 0° C.; after mixing with a larger volume of water, and washing the precipitate with water and then with alcohol, it is dissolved in ether-alcohol, and again precipitated with water, when it is obtained pure.

This nitrate is insoluble in alcohol, but dissolves readily in ether-alcohol, and slightly in acetic acid. Strong potash solution converts this nitrate into the di-nitrate $C_{12}H_{18}O_8\ (NO_3)_2$. [Eder.]

The tetra- and tri-nitrates (collodion pyroxyline) are generally formed together when cellulose is treated with a more dilute nitric acid, and at a higher temperature, and for a much shorter time (13 to 20 minutes) than in the formation of the hexa-nitrate. It is not possible to separate them, as they are soluble to the same extent in ether-alcohol, acetic-ether, or wood spirit.

On treatment with concentrated nitric and sulphuric acid, both the tri- and tetra-nitrates are converted into penta-nitrate and hexa-nitrate. Potash and ammonia convert them into di-nitrate. [Eder.]

Cellulose di-nitrate, $C_{18}H_{13}O_8\ (NO_3)_2$ is formed as a product of partial saponification by the action of alkalis on the higher nitrates, and also by the action of hot dilute nitric acid on cellulose. The di-nitrate is very soluble in alcohol-ether, acetic-ether, and in absolute alcohol. Further action of alkalis on the di-nitrate results in a complete decomposition of the molecule, some organic acids and tarry matters being formed. [Eder.]

By the graduated action of alkaline hydrates on the nitrates previously dissolved, hydroxypyruvic acid is obtained as a main product. [W. Will.]

Technical Applications.—The nitrates of cellulose, as such, are the basis of extremely important industries, and of very opposite character, viz. (1) the production of explosives both for military and industrial use, and (2) as a structural material in the production of xylonite and celluloid, both in the form of compact solids and in sheet or film. The latter uses depend upon the ease with which the nitrates are brought into a plastic condition, or entirely dissolved in various 'neutral' solvents, e.g. alcohol-ether, acetone, amyl acetate. In association also with camphor and vegetable oils (castor oil) their plastic qualities are considerably heightened.

In later years the nitrates have been used as a means of obtaining an artificial cellulose fibre: the solutions of the nitrate being drawn or spun into water as a precipitating solution or into air and the thread is afterwards 'denitrated' by treatment with ammonium sulphide. The resulting product is a practically nitrogen-free cellulose. It is known as artificial silk, or by the more appropriate term, lustra-cellulose.

Cellulose Acetates.—Certain of the polyhydric alcohols, e.g. glycerin, unite directly with acetic acid to form acetic esters. Cellulose, however, is indifferent to acetic acid under any conditions of action so far investigated. Neither does it react with the *anhydride* of the acid at its boiling point; but at 180°, in contact with six times its weight of the anhydride, it is converted into the triacetate (Schutzenberger). With twice its weight of the anhydride, on the other hand, a mixture of lower acetates is obtained, insoluble in glacial acetic acid. The triacetate is freely soluble in the acid. The solutions are highly viscous and are filtered with extreme difficulty. Passage through filter paper is facilitated by dilution with chloroform and benzene. The acetate is soluble, as are all the esters of cellulose, in nitro-benzene. The cellulose regenerated from the thiocarbonate solutions, it is to be noted, reacts with the anhydride directly, passing gradually into solution in the anhydride at its boiling point. The product appears to be the tetracetate. The fibrous celluloses of straw and esparto are also partially acetylated under these conditions.

Reaction of the normal cotton cellulose with acetic anhydride, at the boiling point of the latter, is determined by the addition of zinc chloride in relatively minute proportion (Franchimont); probably, however, as the result of a previous hydrolysis of the cellulose. Iodine has also been found to determine the reaction.

The most characteristic acetylation of cellulose, however, is the following:—The cellulose regenerated from the thiocarbonate is, after purification, mixed with the molecular proportion of zinc or magnesium acetate $[C_6H_{10}O_5 : Zn(O.C_2H_3O)_2]$ in concentrated solution, the mixture dried down on the water-bath, and finally dehydrated at 105°. It is then moistened with acetic anhydride, and acetyl chloride is added in the proportion of $2 \cdot C_2H_3O \cdot Cl$. Reaction ensues at 30–50°, the mass liquefies, and the formation of cellulose tetracetate results. The pure product is obtained as an opaque, white, voluminous powder, soluble in acetic acid and chloroform, to solutions of high viscosity which, on evaporation in thin layers, leave the acetate in the form of transparent coherent film. On boiling these films with normal sodium hydrate diluted with an equal volume of alcohol, the ester is resolved into acetic acid (soluble as sodium acetate) and cellulose (insoluble). The cellulose is obtained as a transparent coherent film. This is an important criterion of a true cellulose acetate, as distinguished from acetates of derivatives of lower molecular weight; the latter giving brittle films which are more or less disintegrated by the process of saponification, and also yield a proportion of soluble carbohydrates, reducing cupric oxide in alkaline solution.

Technical Applications.—The acetates have only recently been prepared on the manufacturing scale. Their physical properties are very similar to those of the nitrates; they are, however, non-explosive and withstand a temperature of 200°. It appears, therefore, that they are capable of substituting the nitrates in many of their useful applications other than as explosives, and with greatest advantage when the properties of an explosive or high inflammability are not merely superfluous but prejudicial.

Cellulose Benzoates.—Esters containing the radical of benzoic acid are obtained by inter-action of the alkali celluloses with benzoyl chloride in presence of excess of the solution of alkaline hydrates.

(*a*) *Mercerised Cellulose.*—The benzoates obtained from the alkali cellulose in this form retain the fibrous structure of the original cellulose. A mixture of products is obtained, varying in composition from a mono- to di-benzoate.

(*b*) *Soluble Alkali Celluloses.*—These react in a more definite way: the products are purified by dissolving in glacial acetic acid, filtering from residues of unattacked celluose, and reprecipitating by water. Thus isolated, the benzoates approximate in composition to $C_6H_8O_3 < \begin{matrix} O.C_7H_5O \\ O.C_7H_5O \end{matrix}$, i.e. to di-benzoate. The benzoates have been but little studied, and at present they have a purely theoretical interest.

Cellulose-Sulphuric Acids.—The solution of cellulose in concentrated sulphuric acid is attended by combination, which may be formulated as under:—

$$C_6H_8O_3\left\{\begin{matrix} OH \\ OH \end{matrix}\right\} + \begin{matrix} H.SO_4H \\ H.SO_4H \end{matrix} = \begin{matrix} H_2O \\ H_2O \end{matrix} + C_6H_8O_3.(SO_4H)_2.$$

The compound is described by Stern—the author of the most recent contributions to the subject—as 'cellulose' disulphuric acid'; but it has not been determined that the compound is a true cellulose derivative. It is more than probable that the original cellulose molecule is simultaneously resolved. The compound may be isolated in the form of its barium salt, $C_6H_8O_3(SO_4)_2Ba$, which is insoluble in alcohol.

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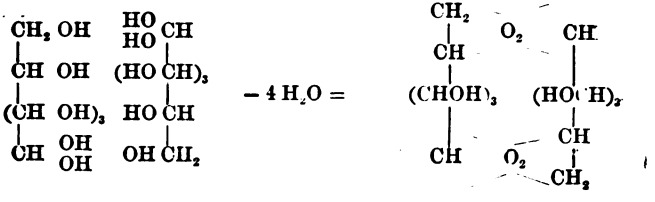
* A. L. Stern, Journ. Chem. Soc., 1895, i., 74–90.

The formation of a derivative of this formula is the first stage in a complicated process of resolution of cellulose, which in many respects resembles that of starch by hydrolytic agents. The ultimate product in both cases is dextrose.

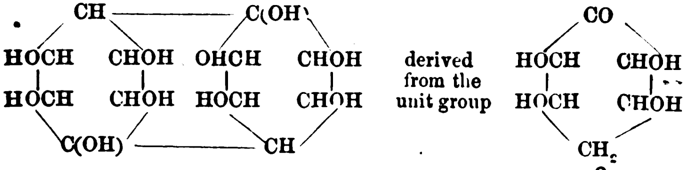
Constitution of Cellulose.—What we have now set forth with regard to the typical cellulose as a chemical individual, is the basis of all we can be said to know of its molecular constitution. Its resemblance to starch consists (1) in the identical empirical formula $C_6H_{10}O_5$; and (2) in both being resolved by ultimate hydrolysis into dextrose groups, which fact is represented by an aggregate formula $n[C_6H_{10}O_5]$. But whereas starch is resolved by enzyme action in such a way that the stages of hydrolysis can be accurately followed, cellulose requires severe treatment, the hydrolysis being complicated by reactions which make it impossible to graduate the changes.

It is essential to give expression to these fundamental differences. The behaviour of starch implies that the linking of the aldose groups is by way of the typical carbonyl oxygen; whereas in cellulose we may very well assume a carbon-to-carbon type of condensation.

Thus, to form a polysaccharide of the starch type, the dextrose molecules would condense as under:—



The cellulose type may be formulated by contrast:—



which unit group fairly generalises the reactions of cellulose, i.e. chiefly (1) the formation of a tetracetate; (2) the reactions with alkalis in which two OH groups take part. The reaction with nitric and sulphuric acids, in which a lesser proportion of OH groups take part than in (1), are explained by the highly 'negative' function of the acid radicals combining and by probable attendant condensations.

It would convey a false impression to attempt to represent the constitution of cellulose more closely. In systematic chemistry, a constitutional formula is justified by the synthesis of the compound from components of known structure: this criterion is necessarily wanting in the case of cellulose, as it is also in that of starch. The synthesis of both compounds has so far only been observed in or by the living cell. Two more simple cases of cellulose synthesis may be noted, in which its formation takes place directly from the crystallisable sugars.

(1) As a result of a change which is set up 'spontaneously' in beet juice, a white insoluble substance is formed and separated in lumps or clots: this substance has all the characteristics of cellulose. After separating this substance, the solution gives with alcohol a gelatinous precipitate resembling the hydrates of cellulose previously described.*

(2) The 'vinegar plant' takes a membranous form which, under microscopic examination, is seen to be clearly differentiated from the zoogloea form of the *Bacterium Aceti.*† It is, in fact, composed of bacterial rods of two μ length contained in a membranous envelope. This envelope has the properties and composition of cellulose. Pure culture of the organism placed in solutions of levulose, mannitol and dextrose reproduce the growth in question, i.e. of the bacteria enveloped in a 'collecting medium' of cellulose. The proportion of cellulose formed to the soluble carbohydrate disappearing, is highest in the case of levulose. The

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* E. Durin, Compt. Rend., 82, 1078; 83, 128.

† A. J. Brown, Journ. Chem. Soc., 49, 432.

cellulose, however, when hydrolysed by sulphuric acid, gives a dextro-rotary sugar. This fact contains a suggestion that the oxygen in cellulose is of ketonic type or function.

Up to the present, in the outline which we have given of the chemistry of the typical cellulose, we have been chiefly concerned with its OH groups; considered broadly, we have studied the compound from the one aspect of its relationship *to water*. As a substance playing an enormously preponderating part in the plant world, its relationship *to oxygen*, i.e. generally to oxidising agents, is of equal importance, since the chemistry of our planet is obviously a 'water and oxygen' chemistry.

We note, in the two succeeding sections, the more important destructive actions determined by oxidising agents and water (hydrolysis).

Decompositions of Cellulose by Oxidants.—It has been already pointed out that cellulose is comparatively resistant to the action of oxidants; that most of the processes for isolating or purifying (bleaching) cellulose depend, *per contra*, upon the use of oxidising agents, which readily attack the 'impurities' with which it is combined or mixed in raw fibrous materials. The cellulose resists the action of these oxidising agents, and, further, withstands in a high degree the action of atmospheric oxygen. It is this general inertness of the compound which marks it out for the unique part which it plays in the vegetable world and in the arts.

It must be again noted that this high degree of resistance to hydrolysis (alkaline) and oxidation belongs only to cotton cellulose and to the group of which it is the type, and which includes the celluloses of flax, rhea and hemp. A large number of celluloses, on the other hand, are distingushed by considerable reactivity, due to the presence of 'free' CO groups, and are therefore more or less easily hydrolysed and oxidised. The 'celluloses' of the cereal straws and esparto grass are of this type, and hence the relative inferiority of papers into the composition of which they enter.*

On the other hand, we have now to study those processes of oxidation to which it yields more or less readily.

A. OXIDATION IN ACID SOLUTIONS.—(1) *Nitric acid* (1·1–1·3 sp. gr.) attacks cellulose at 80–100°, at first slowly then more rapidly, but tending to a limit at which the action again becomes very slow. This limit corresponds with the formation of a characteristic product of oxidation—*oxycellulose*. This subtance, which is white and flocculent, when thrown upon a filter and washed with water, combines with the latter to form a gelatinous hydrate. It requires, therefore, to be rapidly washed with dilute alcohol. It amounts to about 30 p.ct. of the cellulose acted upon, the remainder being for the most part completely oxidised to carbonic and oxalic acids. On ultimate analysis it gives the following numbers:—

$$\left.\begin{array}{ll} \mathrm{C} & 43\cdot4 \\ \mathrm{H} & 5\cdot3 \end{array}\right\} C_{18}H_{26}O_{16}.$$

It dissolves in a mixture of nitric and sulphuric acids, and on pouring into water, the nitrate $C_{18}H_{23}O_{13}(NO_3)_3$ separates as a white flocculent precipitate. From the low number of OH groups reacting with the nitric acid, it may be concluded that the compound is both a condensed as well as an oxidised derivative of cellulose. This oxycellulose dissolves in dilute solutions of the alkalis, and on heating the solutions they develop a strong yellow colour. Warmed with concentrated sulphuric acid it develops a pink coloration similar to that of mucic acid. The compound exhibits generally a close resemblance to the pectic group of colloid carbohydrates.

The by-products of this oxidation are carbonic and oxalic acids, together with the lower nitrogen oxides. The solution, examined at any stage, appears to contain traces only of intermediate products of oxidation of the cellulose. The reaction is divisible into the two stages: (1) the conversion of the cellulose into hydracellulose, evidenced by its breaking down

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* Journ. Chem. Soc., 1894, 472.

to a fine flocculent powder; and (2) the oxidation of the hydracellulose.

The oxycelluloses resulting from this process differ from those formed by the action of CrO_3 (*infra*), in giving small yields only of furfural (2–3 p.ct.) on boiling with HClAq (1·06 sp gr.). It is also to be noted that the carbon is higher than that of the oxycelluloses, giving large yields of furfural (p. 49). These points suggest that, side by side with oxidation, combination of the negative oxy-groups with the more basic groups of unattacked molecules takes place, giving derivatives of the nature of esters. And, indeed, the reaction may be even more complicated. It is clear, from the composition of the nitrate, that the proportion of basic OH groups is reduced to a minimum.

The reaction requires further systematic research in the light of our increased knowledge of the constitution of the simpler carbohydrates and the simple products of their oxidation.

(2) *Chromic acid*, in dilute solutions, attacks cellulose with extreme slowness; in presence of mineral acids oxidation proceeds more rapidly, but at ordinary temperatures is still very slow. The action is, therefore, easily controlled within any desired limit, the oxidation being in this case, of course, directly proportionate to the amount of CrO_3 presented to the fibre. The oxidation is accompanied by disintegration, and the insoluble product is an oxidised cellulose, or oxycellulose, the yield and composition of which bear a simple relation to the amount of oxidation to which the cellulose is subjected. Its properties are similar to those of the oxycellulose above described. It dissolves in a diluted mixture of sulphuric and hydrochloric acids (57 p.ct. H_2SO_4, 5·5 p.ct. HCl), and on diluting and distilling with HCl of 1·06 sp.gr., is decomposed with formation of furfural, $C_4H_3O.COH$, the yield of this aldehyde being proportionate to the state of oxidation of the product.

This is illustrated by the subjoined results of observations:—

Weight of cellulose.	CrO_3 employed.	Yield of oxycellulose.	Yield of furfural p.ct. of oxycellulose.
4·7	1·5	93·0	4·1
4·7	3·0	87·0	6·3
4·7	4·5	82·3	8·2

(Berl. Ber. 26, 2520.)

The first effect of treatment with CrO_3 appears to be that of simple combination; reduction to the Cr_2O_4 then ensues, and the further deoxidation requires the presence of a hydrolysing acid.

From the statistics of the reaction it appears there is little 'destruction' of the cellulose; and, as the oxidation is not attended by evolution of gas (CO_2), we may assume that the reaction consists simply in oxidation with the fixation of water. A certain proportion of the products are dissolved by the acid solution, and of the insoluble residue (oxycellulose) a large proportion is easily attacked and dissolved by alkaline solutions. The product is no doubt, therefore, a mixture; and indeed, it would be hardly conceivable that an aggregate like cellulose should be equally and simultaneously attacked.

The reaction is so perfectly under control that it must be regarded as giving a regulated dissection of the molecule of cellulose, and therefore is an especially attractive subject for exhaustive investigation.

The carbohydrates of low molecular weight are similarly oxidised by chromic acid, and the product of oxidation similarly resolved with formation of furfural.

It is to be noted with cellulose, as with the carbohydrates of low molecular weight, that by oxidation its equilibrium is disturbed in such a way that carbon condensation is easily determined. This fact is of physiological significance, and will be referred to subsequently.

(3) *Of other acid oxidations* which have not been particularly investigated we may mention the action of Cl gas in presence of water, of hypochlorous acid, and of the lower oxides of nitrogen in presence of water. Generally the result of these treatments is similar: the formation of insoluble products having the properties of the oxycelluloses

above described, and soluble products which are oxidised derivatives of carbohydrates of low molecular weight. These, however, are usually obtained in relatively small quantity.

Atmospheric oxidation of cellulose—if it could be proved to take place—would fall in this category, as cellulose surfaces under ordinary conditions of exposure would be found to be normally acid. From the evidence we have of the condition of paper and textiles of the flax group after centuries of exposure to ordinary atmospheric influences, we may conclude that the oxidation of the normal celluloses under these conditions is excessively slight.

B. OXIDATIONS IN ALKALINE SOLUTION.—(1) *Hypochlorites*, in dilute solution (< 1 p.ct.) and at ordinary temperatures, have only a slight action upon cellulose—a fact of the highest technical importance, since hypochlorite of lime (bleaching powder) is the cheapest of all soluble oxidising compounds, and the most effective oxidant of the coloured impurities which are present in the raw cellulose fibres or formed as products of alkaline hydrolysis.

While the normal celluloses withstand these bleaching oxidations, there are many celluloses widely differentiated from the cotton type which are eminently oxidisable, and, at the same time, susceptible of hydrolysis. The 'celluloses' of esparto and straw are of this kind (see p. 49), and the economic bleaching of paper pulps prepared from these raw materials can hardly be expected to follow upon the same lines as that of 'rag' pulp (cotton and linen). A study of the factors involved in the process will be found in a paper entitled 'Some Considerations in the Chemistry of Hypochlorite Bleaching.'[*] These factors are—in addition to temperature and concentration (Cl_2O) of the bleaching solution—the nature of the base in union with the hypochlorous acid, and its proportion to the acid. A knowledge of the operation of these factors will enable the bleacher to control a process which is usually carried out on an entirely empirical basis.

[*] Journ. Soc. Chem. Ind. 1890.

The resistance of cellulose to the action of these solutions necessarily has its limits, and when these are exceeded the fibre-substance is oxidised and disintegrated, and an oxycellulose results. These effects are rapidly produced by the joint action of hypochlorite solutions and carbonic acid. The oxycellulose formed in this way acquiring the property of selective attraction for certain colouring matters—notably the basic coal-tar dyes—its presence in bleached cloth is easily detected by a simple dyeing treatment consisting in immersing the oxidised fabric in a dilute solution (0·5-2·0 p.ct.) of one of these dye stuffs, e.g. methylene blue. Local over-oxidation may be diagnosed in this way with certainty, and bleachers' damages may be thus ascertained and often traced back to the operating cause in the light of this 'oxycellulose' test.[*]

The oxycellulose or disintegrated fibre resulting from this process of oxidation differs but little in empirical composition from cellulose itself, probably owing to the fact that the more highly oxidised products are dissolved in the solution of the oxidant, which is, of course, basic. Its reactions indicate the presence of free CO groups, and it readily undergoes further oxidation by atmospheric oxygen, the oxidation being much accelerated by temperatures over 60°. The OH groups of this oxycellulose are also more reactive than those of the original cellulose, acetylated derivatives being obtained by boiling the product with acetic anhydride.

The facts in relation to the conversion of cotton cellulose into oxycellulose by the action of bleaching powder were first made known by Georges Witz in 1883.

Since then a number of papers have been published dealing with special aspects of the phenomena—theoretical and practical. Of these we may cite: Schmidt, Dingl. J. 250, 271; Franchimont, Rec. Trav. Chim. 1883, 241; Nölting and Rosenstiehl, Bull. Rouen, 1883, 170, 239; Nastjukow, Bull. Mulhouse, 1892, 493.

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[*] Journ. Soc. Chem. Ind. 1884.

[†] Bull. Soc. Ind. Rouen, 10, 416; 11, 169.

It is probable on many grounds that the oxidised products obtained from cellulose by the action of the hypochlorites in the manner described are mixtures of one or more oxycelluloses with residues of unoxidised cellulose. More recent investigation has led to the conclusion that the extreme product of oxidation is an oxycellulose of the empirical formula $C_6H_{10}O_6$, which is freely soluble in dilute alkaline solutions in the cold; and that cellulose oxidised by hypochlorite solutions is a variable mixture of this product with hydracellulose, and unaltered cellulose. (Nastjukow.)

By drastic oxidation of cellulose by the oxyhalogen compounds—i.e. by treatment with chlorine or bromine in presence of alkaline hydrates—the molecule is entirely broken down to the simplest products. With bromine, i.e. hypobromite, some quantity of bromoform is obtained; carbon tetrabromide is also easily obtained and identified.†

(2) *Permanganates.*—The permanganates in neutral solution attack cellulose but slowly, and they may therefore be usefully employed as bleaching agents. In presence of alkalis a more drastic oxidation is determined. The degree of oxidation is, of course, dependent upon the conditions of treatment. The following general account of a particular experiment and its results will illustrate its main features.

22·6 grms. cellulose, with 400 c.c. caustic soda solution; 50 grms. $KMnO_4$ added in successive small portions; temperature, 40–50°. Proportion of cellulose to oxidising oxygen, $2C_6H_{10}O_5 : 7O$.

The main products were—

(α) Oxycellulose . . .	10·5	grms.,	approximately	50 p.ct.
(β) Oxidised carbohydrates in solution . . .	3·5	,,	,,	16 ,,
(γ) Oxalic acid . . .	4·3	,,	,,	20 ,,
(δ) Carbonic acid, water and traces of volatile acids	. . .		,,	14 ,,

(α) The oxycellulose gelatinised on washing and was similar to the product obtained by the action of nitric acid

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* Collie, Journ. Chem. Soc. 65, 262.

(β) The oxidised carbohydrate in solution resembled 'caramel' in appearance. The compound or mixture was precipitated by basic lead acetate, and isolated by decomposing the precipitate with hydrogen sulphide, filtering and evaporating. On distillation from hydrochloric acid, furfural was obtained in large proportions.

(3) *Extreme action of alkaline hydrates.*—When fused at 200–300° C. with two to three times its weight of sodium or potassium hydrates, cellulose is entirely resolved, the characteristic products being hydrogen gas and acetic (20–30 p.ct.) and oxalic (30–50 p.ct.) acids. Generally the reaction takes the same course as with the simpler carbohydrates, resolution of the cellulose into molecules of similar constitution, no doubt, preceding the final resolution, which appears to be an exothermic or explosive reaction.

C. DESTRUCTIVE RESOLUTION BY FERMENT ACTIONS.—This group of decompositions of cellulose is necessarily a very wide one. In the 'natural' world of living organisms, of course, no structures are permanent; and although cellulose distinguishes itself by relative permanence and resistance to the disintegrating actions of water and oxygen, the differentiation in this respect is only a question of degree, and all cellulosic structures are subject to the law or necessity of redistribution.

The directions of redistribution are chiefly three: viz. (1) In the assimilating process of the plant a cellulosic structure is broken down, re-absorbed into the supply of plastic nutrient material, and re-elaborated.

(2) Structures which have ceased to play a part in the general organisation of the plant are cast off, and then exposed as 'dead' matter to the play of the redistributing agencies of the natural world. The processes of 'decay' take various forms, according to the conditions to which they are exposed. The humus of soils, peat, lignite, and all forms of coal present various forms of the residual solid products of the decay of cellulosic structures, the remainder having been dissipated and restored to the general fund of

matter in circulation, in the gaseous form—viz. as CO_2 and CH_4.

(3) In the processes of animal nutrition plants and vegetable substances are, of course, most important factors. In the course of animal digestion the vegetable substances are attacked by the fluids of the alimentary tract and resolved into proximate constituents fulfilling the requirements of the organs of assimilation; and in addition to these decompositions, which are largely hydrolytic in character, more fundamental resolutions are observed in which the carbohydrate molecules are completely broken down, i.e. with formation of gaseous products.

The Cellulose Group.—Thus far we have been dealing mainly with one member of the very numerous class of plant constituents comprehended in the term 'cellulose.' While the properties and characteristics of cotton cellulose are in such wise representative that this substance may be regarded as the typical cellulose, the differentiation of this, as of every other group of tissue constituents, in conformity with functional variation, necessarily covers a wide range of divergencies.

The celluloses of the plant world, so far as they have been investigated from the point of view of chemical constitution, group themselves as follows:—

(*a*) Those of maximum resistance to hydrolytic action, and containing no directly active CO groups.

(*b*) Those of lesser resistance to hydrolytic action, and containing active CO groups.

(*c*) Those of low resistance to hydrolysis, i.e. more or less soluble in alkaline solutions and easily resolved by acids, with formation of carbohydrates of low molecular weight.

GROUP (*a*).—In addition to the typical cotton cellulose—which, it is to be noted, is a seed-hair—there may be included in this group the following fibrous celluloses which constitute the bast of exogenous flowering annuals: viz. the celluloses of *Flax* (Linum usit.), *Hemp* (Cannabis sativa), *China Grass* (Rhea and Boehmeria species), and of the lesser known

Marsdenia tenacissima, *Calotropis* (gigantea), *Sunn Hemp* (Crotalaria juncea).

As in the case of cotton, the celluloses of the fibres are considered in the form of the white (or bleached) and purified residues, resulting from the treatment of raw materials by processes of alkaline hydrolysis and oxidation more or less severe in character. For the purification of the celluloses in the laboratory, the methods usually practised consist in (1) alkaline hydrolysis, i.e. treatment with boiling solutions of sodium hydrate, carbonate or sulphite; (2) exposure to bromine water or chlorine gas; or, when oxidation alone is sufficient for the removal of the 'impurities,' to solutions of the hypochlorites or permanganates (in the latter case followed by a treatment with sulphurous acid to remove the MnO_2 deposited on the fibre-substance); (3) repetition of (1) for the removal of products rendered soluble by (2).

The celluloses of this group thus purified may be taken as chemically identical with cotton cellulose, investigation having so far failed to differentiate them. It must be noted, however, that the several members of the group present distinct morphological characteristics, and differ also in such external properties as lustre and 'feel.' These are correlated with the differences in minute structure, but they are no doubt in part due to differences of substance. So far, however, we have no knowledge of the proximate constitution of these substances, and can therefore say nothing as to the causes of difference in this respect.

On the other hand, the essential identity of these celluloses is established in regard to ultimate composition and in reference to the following properties and reactions:—

(1) Resistance to hydrolysis and oxidation, and other negative characteristics, indicating a low reactivity of the CO and OH groups.

(2) The relationships to the special solvents previously described, including the thiocarbonate reaction.

(3) Formation of esters, nitrates, acetates, benzoates.

Of the above, it is sufficient in general laboratory practice to examine cellulose in regard to ultimate composition, resistance to alkaline hydrolysis, behaviour with solvents, and reactions with sulphuric acid (solution without blackening) and nitrating mixture (H_2SO_4 and HNO_3); the 'nitration' proceeds without oxidation, and gives a higher yield of product, 160–180 p.ct., according to the conditions.

GROUP (*b*).—These celluloses are differentiated from the former group (1) by ultimate composition, the proportion of oxygen being higher; (2) by the presence of active CO groups; (3) in certain cases by the presence of the $O \cdot CH_3$ group.

The general characteristics of the group are those of the *oxycelluloses*. It has recently been shown that these oxidised derivatives of the normal celluloses are further characterised by yielding *furfural* as a product of acid (HCl) hydrolysis. The yield of this aldehyde is, in certain cases, increased by previous treatment of the oxycellulose with a reagent prepared by saturating sulphuric acid of 1·55 sp.gr. with HCl gas. In this reagent the oxycelluloses dissolve; and on then diluting with HCl of 1·06 sp.gr. and distilling, maximum yields of furfural are obtained, the yield being an indirect measure of the increased proportion of oxygen beyond that corresponding with the formula $C_6H_{10}O_5$.

Celluloses of this class are much more widely distributed in the plant world than those of the cotton type; they appear, from recent observations, to constitute the main mass of the fundamental tissue of flowering plants, in which they usually exist in intimate mixture or combination with other groups more or less allied in general characteristics. It appears, from a survey of the contributions of investigators to the subject of cellulose, that research has been very much confined to the fibrous celluloses, more particularly to such as receive extended industrial use. The time has come, however, when systematic research is much needed to establish at least a preliminary classification of the 'cellular' celluloses upon the lines of chemical constitution. Constitution, taken in relation to physiological function, is an attractive subject of research; and it is in the plant cell, where synthetical operations are predominant, that we have to look for the foundations of a 'new chemistry,' which shall definitely investigate the relation of matter to life.

It is to be noted that the differentiation of many of these celluloses from the typical cotton is, in regard to empirical composition, only slight. There appear, on the other hand, to be more important differences of constitution. Thus pinewood cellulose dissolved in sulphuric acid, the solution diluted and boiled, and further treated for the isolation of crystallisable carbohydrates, yields these (i.e. dextrose) in only small proportions.*

Investigation has stopped short at this negative result. It would be of interest, therefore, to isolate the products formed in the reaction with the concentrated sulphuric acid, so as to characterise them, at least generally. Until this is done, or some other method of proximate resolution is worked out in detail, we can only say that the constitution of these celluloses is in some important feature radically different from that of the typical cellulose.

An account of recent investigations of these 'celluloses' will be found in Berl. Ber. 1893, and a more special treatment of the subject, *ibid.* 1894, and Journ. Chem. Soc. 1894 (C. Smith).

Of this group of the natural oxycelluloses, the following have been more particularly investigated:—

(1) *Celluloses from woods and lignified tissues generally.*—Lignified tissues are made up of compound celluloses, to be subsequently described (see 'Ligno-celluloses,' p. 53), from which the celluloses may be isolated by a number of treatments, all depending upon the relative reactivity of the so-called 'non-cellulose' constituents, which in combination with the celluloses make up the compound cellulose, ligno-cellulose or wood-substance. These non-cellulose constituents are readily attacked and converted into soluble derivatives; and there are various industrial processes for preparing

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* Lindsey and Tollens, Lieb. Ann. 267, 370.

celluloses (paper pulp) from raw materials of this class, depending upon the direct conversion of the former into such soluble compounds. The isolated celluloses show the following general characteristics:*—

Elementary composition $\left\{\begin{array}{l} \text{C } 42\cdot8\text{–}43\cdot8 \text{ p.ct.} \\ \text{H } 5\cdot6\text{–}5\cdot9 \text{ ,,} \end{array}\right.$ *Yield of furfural*, by solution and hydrolysis (HCl), 2–6 p.ct. *Reactions* with phenylhydrazine salts and magenta-sulphurous acid, indicating the presence of active CO groups. These celluloses are necessarily less resistant to oxidation and hydrolysis, but show in all other respects a close general agreement with the normal cotton cellulose.

(2) *Celluloses from cereal straws, from esparto, etc.*—These celluloses are isolated from the matured stem or haulm, by digestion with alkaline lye at elevated temperatures. They are also of considerable industrial importance, being largely used in the manufacture of the cheaper kinds of writing and printing papers.

Recent investigation has shown that these celluloses are strongly differentiated from the normal, and are, in fact, pronounced oxycelluloses. The following are the characteristics of difference:—

Ultimate composition, after treatment with hydrofluoric acid, to remove siliceous ash constituents:—

	Oat straw cellulose.		Esparto cellulose.	
	(1)	(2)	(1)	(2)
C	42·4	42·4	41·78	41·02
H	5·8	5·8	5·42	5·82

Yield of furfural by solution and hydrolysis (HCl):

Oat straw cellulose.	——	Esparto cellulose.
12·5		12·2

Reactions.—In addition to those with Fehling's solution, phenylhydrazine salts, and magenta sulphurous acid indicating the presence of active CO groups, the celluloses give a characteristic rose-red colouration on boiling with solutions

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* Berl. Ber. 27, 161.

of aniline salts. This reaction serves to identify their presence in papers, and from the depth of the colouration the percentage may be approximately estimated.

Investigation has also established the following points in regard to the oxidation and deoxidation of these oxycelluloses.

They are gradually oxidised in dry air at the temperature of the water-oven, undergoing discoloration; the yield of furfural by hydrolysis showing a progressive increase. They are deoxidised, on the other hand, by neutral and alkaline reducing agents. Thus, after lengthened exposure to solutions of zinc-sodium hyposulphite, prepared by the action of zinc dust upon sodium bisulphite, the yield of furfural—which is a measure of the degree of oxidation—was reduced, in the case of esparto cellulose, from 12·6 to 8–9 p.ct.

A still further deoxidation results from solution of these oxycelluloses as thiocarbonate, and regeneration of the cellulose by heating the solution at 80–100°. The regenerated cellulose approximates to the normal, yielding only 2 p.ct. furfural on hydrolysis. It is to be noted, however, that esparto cellulose, in common with all the celluloses of this group, is partly hydrolysed to soluble derivatives by this treatment; the regenerated cellulose amounting to 80 p.ct. of the original weight dissolved. The soluble portions yield furfural on hydrolysis, amounting (in a typical experiment) to 4·0 p.ct. of the original.

The celluloses of this group are dissolved by concentrated sulphuric acid to dark-coloured solutions. On diluting and boiling, they are resolved into carbohydrates of low molecular weight; dextrose appears to be invariably formed, and in many cases also mannose; but only very small yields of either carbohydrates have been so far obtained.

GROUP (c).—This includes the heterogeneous class of non-fibrous celluloses which we have defined as of low resistance to hydrolysis, being easily resolved by boiling with dilute acids, and being also more or less soluble in dilute alkaline solutions. This group has been but little studied and therefore can only be generally characterised. Physiological research has shown that there are a large number of cellular, as distinguished from fibrous 'celluloses,' which are readily broken down (hydrolysed) by the action of enzymes within the plant itself, whether as a normal or abnormal incident of growth. Thus, in the germination of starchy seeds, the cell walls (cellulose) of the starch-containing cells are broken down, as a preliminary to the attack upon the starch granules themselves, to form the supply of nutrition to the embryo. In an exhaustive investigation of the germination of the barley, Brown and Morris have thrown a good deal of light upon this particular point, which they emphasise in the following words: 'that the dissolution of the cell wall invariably *precedes* that of the cell contents during the breaking down of the endosperm is a fact of the highest physiological importance, and one which for the most part has been strangely overlooked.'

A similar, but abnormal, dissolution of cell walls is that which occurs in the attacks of parasitic organisms upon the tissues which they invade.

These processes are well known to physiologists, who, however, generally regard 'cell wall' and 'cellulose' as substantially identical terms. The chemical differentiation of the substances comprising cell walls is, on the other hand, an entirely new field of research; but, although investigation has not gone very far, the results are sufficient to show that the celluloses of this order are enormously diversified. The variations already disclosed are (1) those of the carbohydrates yielded by ultimate hydrolysis, and (2) those of molecular configuration or condensation. We have already seen that the celluloses of the cotton group (*a*) yield dextrose as the ultimate product of hydrolysis; those of group (*b*) yield, in addition to dextrose, mannose and probably other bodies; and the group we are at present discussing yield, in addition, galactose, and the pentoses xylose and arabinose. In illustration we may cite a few examples. Thus GALACTOSE has been obtained as a product of hydrolysis of the cell walls of the seeds of Lupinus luteus, Soja hispida, Coffea arabica, Pisum sativum, Cocos nucifera, Phœnix dactylifera, etc. MANNOSE is obtained in relatively large quantity from the 'ivory nut,' and from a very large number of other seeds; and PENTOSES, from the seeds of the cereals and of leguminous plants. It appears, therefore, generally that a large number of plant constituents which have been denominated by the physiologists as 'cellulose' have little more title to be considered as such than has starch. However, external resemblances count for something, at least in the beginnings of classification, and substances of the type we are considering may be conveniently grouped with the celluloses; but we should propose to apply to them the term PSEUDO-CELLULOSES, or HEMICELLULOSES—as has been proposed by E. Schulze. Our group (*c*) of pseudo-celluloses may therefore be defined as substances closely resembling in appearance the true celluloses, but easily resolved into simple carbohydrates by the hydrolytic action of enzymes, or of the dilute acids and alkalis.

Compound Celluloses.—In dealing with the isolated celluloses, it has been shown that the processes by which they are isolated or purified are based upon the relative reactivity of the compounds with which the celluloses are combined or mixed, in the raw or natural products of plant life. These natural forms of cellulose are, of course, multitudinous. Remembering the infinite variety of the vegetable world, the endless differentiation of form and substance of the tissues of plants, it might be presumed that the chemical classification of these products would present unusual complications.

Investigation, however, has shown, and continues to show, that this great diversity of substance, as revealed by proximate analysis, exists upon a relatively simple chemical basis. The compounds constituting the fundamental tissue of plants may, in fact, be broadly classified in correspondence with the three main types of differentiation of the cell wall long recognised by the physiologists, viz. *lignification*, *suberisation* and conversion into *mucilage*. That is to say, in addition to the celluloses proper and hemi- or pseudo-celluloses—which may be defined as polyanhydrides of the normal carbohydrates, ketoses and aldoses—there are three main types of *compound* celluloses in which the celluloses as thus defined exist in combination with other groups, as follows:—

LIGNOCELLULOSES.—The substance of lignified cells and fibres, notably the woods—of which the characteristic *non-cellulose* constituent is a R. hexene derivative.

PECTOCELLULOSES AND MUCOCELLULOSES.—Comprising a wide range of tissue constituents—of which the non-cellulose constituents are colloidal forms of the carbohydrates, or closely-allied derivatives, easily converted by hydrolytic treatments into soluble derivatives of lower molecular weight, and belonging to the series of 'pectic' compounds, or hexoses, etc.

ADIPOCELLULOSES AND CUTOCELLULOSES.—The substance of cuticular and suberised tissues—in which the cellulose is associated with fatty and waxy bodies of high molecular weight.

Of the above groups, the first only has any direct interest to the paper-maker. The ligno-celluloses *as such* are in the forms of the jute fibre and 'mechanical' pulps, actual components of papers of certain classes; the pectic and cuticular constituents of fibrous raw materials are almost entirely eliminated by the chemical and mechanical methods of treatment of such materials, of separating and preparing the actual paper-making fibres.

LIGNOCELLULOSES.—As the chemical prototype of the substance of lignified tissues, we select the jute fibre. This fibre is the isolated bast tissue of plants of the species Corchorus (order *Tiliaceæ*) an annual of rapid growth, attaining a height of 10–12 feet in the few months required in the Indian climate for the maturing of the plant. The textile fibre or bast is obtained in long strands. It is of a brown to silver-grey colour in the finer sorts.

The jute *fibre substance* differs strikingly in composition and reactions from the celluloses. Its ultimate composition is represented by the percentage numbers:—

		Calc. for $C_{12}H_{18}O_9$.
C	46·0–47·0	47·0
H	6·1– 5·8	6·0
O	47·9–47·2	47·0

The above numbers are calculated to dry ash free substance. In the air-dry condition the fibre contains on the average 10·0 p.ct. moisture; the normal ash amounts in the aggregate to about 1·0 p.ct.

Reactions.—It is differentiated from the celluloses by the following characteristic reactions. With solutions of *aniline salts* (and other coal tar bases) it gives a deep yellow colouration. With *phloroglucinol* dissolved in hydrochloric acid (1·06 sp.gr.) it gives a rose-red colouration: the red solution of ferric ferricyanide is reduced with production of 'prussian' blue which is deposited in the fibre-substance; a solution of magenta discolorised by sulphurous acid dyes the fibre a deep magenta colour, a reaction which is characteristic of aldehydes and ketones. The jute fibre is also dyed directly by a large variety of the 'coal tar' dyes.

But the most characteristic of its reactions is that of direct combination with the halogen elements, and notably chlorine. The combination is attended with change of colour to bright yellow; the yellow quinone chloride (*infra*) is dissolved by a solution of sodium sulphite, with development of a magenta-red colouration.

While serving thus as a qualitative reaction for the identification of the lignocellulose, it is also one which takes place in definite quantitative proportions. Further, when so carried out, it affords a sharp separation of the lignocellulose into its constituent groups: viz. (1) the *lignone* (ketone) which combines with the chlorine and may then be dissolved away by sodium sulphite solution, leaving (2) the *cellulose* constituents of the fibre-substance, having the properties of the celluloses of group (2) of the classification on p. 49.

From its critical importance the process of chlorination of the jute lignocellulose will be described in detail. The fibre is prepared by a preliminary treatment with a boiling solution of sodium hydrate (1 p.ct. NaOH). From this it is well washed and squeezed to retain not more than its own weight of water. In this condition it is exposed for one hour to an atmosphere of washed chlorine gas. The fully chlorinated fibre is washed to remove the hydrochloric acid formed in the reaction, and transferred to a solution of the sulphite (1–2 p.ct. Na_2SO_3) in which it is boiled. To complete the isolation of the cellulose, the solution is made alkaline with sodium hydrate (0·2 p.ct. NaOH), after which the boiling is continued 2–3 minutes. The fibrous mass is thrown on a cloth filter, and thoroughly washed. This residue is the almost pure *cellulose*; and the entire elimination of the *non-cellulose* components of the original fibre, is shown by failure to react with the various reagents previously cited

The following are important quantitative data. The yellow chlorinated derivative has the empirical formula $C_{19}H_{18}Cl_4O_9$; to form this derivative the fibre-substance (purified and prepared by the boiling with alkali) takes up 8 p.ct. of its weight in *combination*; at the same time an equal amount goes to form hydrochloric acid. The proportion of cellulose yielded is approximately 80 p.ct. This cellulose is a mixture of two celluloses, *a cellulose* resembling the normal cotton cellulose, and *β cellulose*, a furfural-yielding cellulose, and much less resistant to hydrolytic treatments, both acid and alkaline. In other processes of attacking the fibre for the isolation of cellulose, this latter is hydrolysed and dissolved, and the yield falls to 62–66 p.ct.

Bromine acts similarly, but its action is relatively slow and incomplete. Thus if the fibre prepared by boiling in weak alkalis is submerged in saturated bromine water, it requires some hours at the ordinary temperature for the fibre-substance to combine with the maximum proportion of the halogen. The brominated product is similarly attacked and dissolved by alkaline solutions; but it will be found that the treatment requires to be once or twice repeated before the isolation of cellulose is complete. In certain cases, however, the method is useful as an alternative process of isolating and estimating cellulose, not only in jute, but in other fibrous materials.

Iodine is absorbed by the ligno-celluloses from aqueous solutions, and they are coloured a deep brown. The absorption is constant, under constant conditions of treatment, and as a result of quantitative investigations, it was established that in digesting the fibre-substance at 18° C., with twenty times its weight of the $\frac{N}{10}$ iodine solution (in potassium iodide) the absorption is constant at 12·9–13·3 p.ct.

No definite compound is formed, however, and the halogen is easily removed by solvents.

These reactions with the halogens, and notably with chlorine, are dealt with thus prominently, as they are specifically characteristic of the lignone or non-cellulose group, the presence of which in combination with the cellulose is the distinguishing feature of this class of compound celluloses. The lignone group is sharply differentiated from the carbohydrates by its reactions, which are those of an unsaturated compound. Investigation of the chlorinated derivative has established it as a *quinone chloride* and related to the trihydric phenol pyrogallol, yielding as it does trichloropyrogallol on reduction. Subordinate characteristics of the lignone complex are the presence of methoxyl groups $(O \cdot CH_3)$, and the absence of reactive hydroxyl (OH) groups. It must be noted that the union of cellulose and lignone to form the ligno-cellulose complex is very intimate, and in several characteristic reactions both of decomposition and synthesis, the ligno-cellulose behaves as a homogenous compound. Of such we may cite more particularly the actions of hydrolytic agents under ordinary conditions on the one hand, and reactions of 'nitration' and 'acetylation' on the other. The highly reactive nature of the lignone group exposes it, on the other hand, to selective attack not only by the halogen as described, but by dilute nitric acid at temperatures of 50° and upwards, and by sulphurous acid and the bisulphites at elevated temperatures, all leading consequently to the isolation of the more resistant cellulose.

We must briefly note here the structural relationship of the jute-cellulose to the jute-fibre. The cellulose is obtained in the form of single, ultimate, bast fibres or cells, of short length (2 mm. = $\frac{1}{12}$ inch); whereas, the jute-fibre occurs in apparently long strands. The latter are, however, in effect complex, and a cross-section viewed under the microscope reveals a number of the unit cells in close apposition. It would appear therefore that these fibre-bundles owe their cohesion to the *lignone* constituent; and hence the term '*encrusting and intercellular substance*' by which it is frequently designated. This view is at variance with the undoubted chemical homogeneity of the fibre-substance; and the student must avoid any so crude a view of a lignocellulose, as of pure cellulose 'overlaid' or 'encrusted' with its lignone or non-cellulose components.

The remaining features of the chemistry of the typical lignocellulose we note only briefly.

Action of Cellulose Solvents.—The lignocellulose is attacked and dissolved similarly to the celluloses, by zinc chloride in concentrated solution, whether in water or hydrochloric acid: so also by solutions of cuprammonium. The solution is attended by hydrolysis, which is greater or less according to the conditions and duration of the action: by precipitation of the solutions the recovery of the lignocellulose is therefore incomplete. The lignone groups are found in both soluble and insoluble fractions,.

Action of Hydrolytic Agents.—(1) *Alkaline solutions* at temperatures of 60–100° attack the lignocellulose as a whole, dissolving a proportion of the fibre-substance from 10–25 p.ct., according to the nature of the alkali, the concentration of the solution and the temperature and duration of its action. With caustic soda solution (of 3 p.ct. Na_2O) at elevated temperatures (150–170°), the lignone and β cellulose groups are selectively attacked, and a cellulose is isolated approximating in composition to the normal celluloses.

Concentrated solutions of caustic soda (12–25 p.ct. Na_2O) in the cold determine a 'mercerising' action, attended by a remarkable change in appearance due to partial resolution of the fibre-bundles, and the swelling of the individual fibres. These hydration effects are accompanied by a partial conversion into soluble derivatives (10–15 p.ct.) but there is no essential change in the composition of the lignocellulose.

(2) *Acids.*—The dilute 'mineral' acids, e.g. HCl and H_2SO_4 of semi-normal strength rapidly disintegrate the fibre at temperatures exceeding 60°. As the action continues the fibre takes a mahogany-red colour and falls to a mass of brittle fragments, harsh to the touch. The acid solution acquires a reddish-yellow colour and smells strongly of acetic acid: this acid is in effect produced in some quantity. The furfural-yielding groups of the lignocellulose yield more readily to these actions, and when the lignocellulose is digested with 1 p.ct. sulphuric acid at 3 atm. pressure, they are entirely hydrolysed and dissolved. The insoluble fibrous residue gives the characteristic reactions of the original fibre, i.e. the essential features of its lignone constituent are not changed.

Dilute Nitric Acid at 50–80° has a specific and selective action upon the lignone group; from which soluble yellow coloured nitroso-ketones are formed, the β cellulose is simultaneously hydrolysed, and finally the α cellulose is isolated. This reaction is characteristic, and has been more closely studied with the related group of lignocelluloses, the hard woods.*

Sulpho-carbonate Reaction.—The joint and simultaneous action of carbon disulphide, and the alkaline hydrates e.g. solutions of 15–20 p.ct. NaOH, produces only a partial conversion of the constituents of the fibre into sulpho-carbonates, the proportion actually passing into solution on subsequent treatment with water varying from 25–50 p.ct.

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* E. C. C. Baly and J. C. Chorley, Berl. Ber. 195, 922.

according to the conditions of treatment. The reaction is remarkable for the extreme degree of hydration and gelatinisation of the portion which does not actually dissolve: in the swollen and gelatinised condition it has been observed to occupy 100 times the volume of the original. In this reaction it is the group we have designated as β cellulose which yields most readily, and is, in fact, dissolved. The undissolved residue reacts with chlorine as does the original lignocellulose.

Compounds with Acid Radicals. *Esters.*—Of these, the nitrates are alone of sufficiently definite composition to be considered as derivatives of the entire ligno-cellulose.

The nitrates are obtained by short exposure to the action of the mixed acids ($HNO_3 + H_2SO_4$); with concentrated nitric acid alone, rapid and destructive oxidation supervenes. The highest yield of nitrate obtainable has been determined at 145 p.ct. of the original lignocellulose: this increase of weight would correspond with the production of a tri-nitrate of the formula $C_{12}H_{15}O_6.(NO_3)_3$. The percentage of nitrogen in the products is from 11·8 to 12·2, and this indicates the production of a tetra-nitrate. This discrepancy is accounted for by secondary reactions—with production and removal of water molecules. The nitrates are of a brilliant yellow colour and are homogeneous in composition, fractional solution failing to resolve them, as would be the case if they were mixtures of cellulose nitrates, with derivatives of the lignone group. In explosive properties, and in their behaviour towards solvents, they closely resemble the cellulose nitrates.

Compound with other acid radicals, e.g. acetates and benzoates, have been obtained, but they are of an ill-defined character,

Action of Oxidising Agents.—As 'unsaturated' compounds, i.e. containing unsaturated groups, the lignocelluloses are relatively greedy of oxygen. Also it is evident that the lignone groups yield more readily to such actions than the cellulose constituents of the fibre. Thus by the action of chromic acid in dilute solution and in presence of sulphuric acid the former may be entirely eliminated. The most important oxidations, however, are those of the 'standard' bleaching agents—the permanganates and hypochlorites. By a careful regulation of the conditions, the jute fibre may be bleached by these reagents to a very high point, but by no means to the pure white of a cellulose. The *lignocellulose* is essentially a coloured compound, and in attempting to exceed the limit which this imposes, we merely remove the lignone groups and approximate to the condition of cellulose. This implies loss of weight, and for the reasons given above, loss of strength by actual disintegration of the fibre-bundles.

As the products of oxidation of the fibre substance are acid in character, precautions must be taken in employing the hypochlorites, that the bleaching solutions do not become acid: in that case hypochlorous acid is set free and the lignone groups are *chlorinated.* The presence of the resulting chlorinated derivatives in paper or textiles is extremely prejudicial.

The lignocelluloses, of which we have briefly described the typical jute-fibre, are of course widely distributed in the plant world, and are the components of structures of various function. We may instance as ligno-celluloses of closely related composition and constitution, the hard or stony concretions of the pear: and, again, the most important constituent of the juice of the white currant, a type of soluble and hydrated lignocelluloses, of which group it has all the essential characteristics. This latter is a further proof that the lignocelluloses, though complex, are homogeneous. But the most widely distributed of the ligno-celluloses are the woods: in this group a surprising unity of chemical type is preserved; and though a woody stem is made up of cells and vessels of various structure and function, we may regard them as composed of an identical chemical substance. In the woods proper, all those features of the typical lignocellulose, which it has in contrast to cellulose, are more strongly developed. This is readily seen by a comparison of a typical wood, viz. beech-wood, with the jute-fibre in regard to the essential chemical constants :—

—	Elementary Composition.	Proximate resolution.		Quantitative Reactions of Non-cellulose.		
	Carbon.	Cellulose.	Non-cellulose.	Methoxyl.	Furfural.	Cl. Combining.
Jute . .	46·5	75	25	4·0	8·2	8·0
Beech .	49·1	55	45	6·2	12·8	12·0

Remembering that the woods are the substance of perennial stems, whereas the lignocelluloses previously dealt with occur in or as 'annual' structures, these numbers contain the suggestion that the process of *lignification* consists chemically in the production of the unsaturated lignone groups at the expense of cellulose. This view is emphasised by the progressively 'condensed' character of the union of the groups, which shows itself in the relatively strong resistance of the woods to all processes of simple hydration and hydrolysis. This is most clearly seen in relation to the solvents of cellulose: for while jute and the 'annual' lignocelluloses are similarly dissolved, the woods yield to no process of solution as a whole. More definitely characteristic is their complete resistance to the thiocarbonate reaction; which argues the absence of reactive OH groups. This, again, is confirmed by the results of conversion into nitrates by the action of nitric acid in presence of sulphuric acid, which are so imperfect and unsatisfactory that this group of lignocelluloses cannot be said to be 'nitrated' as such, but yield only as the result of partial resolution into constituent groups. A little reflection will show that inertness in these directions is an important condition of such 'permanent' functions as the woods are destined to fulfil.

But in all other respects there is the closest similarity between the two groups of lignocelluloses. The specific colour reactions are shown by the woods in greater intensity proportioned to their higher proportion of unsaturated (lignone) groups, thus:—

(*a*) Golden yellow, with solutions of salts of aniline, etc.

(*b*) Carmine-red, with solutions of phloroglucinol in HCl (1·06).

(*c*) Magenta, due to liberation of this colouring matter from its solutions decolorised by sulphurous acid.

(*d*) Prussian blue, 'reduced' from solutions of ferric ferricyanide.

Further, the characteristic reactions with chlorine and bromine, due to their combination with lignone groups.

The reaction with solutions of *dimethyl-paraphenylenediamine* we may mention more particularly, as it is the basis of a method of estimating the proportion of these *lignocelluloses* in a paper. The woods are prepared by a *mechanical* process of wet grinding, for working up into papers of a certain kind and quality (p. 147), in which therefore they are present in their 'natural' or undecomposed form. With this particular base they give a deep red coloration; and in any mixture with a substance such as cellulose giving no such reaction, the depth of colour is proportional to the percentage of the lignocellulose in the mixture. With a series of standard mixtures, i.e. of known composition, a comparison is at once instituted determining the composition of a given specimen. This test was devised by C. Wurster, who further simplified it by preparing test papers containing the reactive base which are moistened and pressed upon a sample to be tested. The colour developed is compared with a scale of chromo-printed stripes representing the colour produced with 10, 20 . . . . 100 p.ct. of the lignocellulose.

We have seen that the condition of combination of these constituent groups prevents the woods reacting as a homogeneous compound. The chemistry of these substances, therefore, is based chiefly on a study of their decompositions, of which the most important are those which yield the cellulose in a pure form. We give, therefore, a brief survey of these processes.

Laboratory Methods. (1) ACTION OF HALOGENS.—The wood is prepared in fine shavings, boiled out in dilute alkaline solutions (1 p.ct. NaOH), washed and exposed to chlorine gas or saturated bromine-water in the cold. The resulting compound of lignone and halogen is dissolved away by a solution of sodium sulphite as described on p. 55. The treatment is repeated until a pure cellulose is isolated.

A series of determinations by Hugo Müller gave the following percentages of cellulose in representative woods :—

——	Birch.	Beech.	Ebony.	Oak.	Poplar.	Fir.	Pine.
Cellulose p.ct.	55·5	45·5	30·0	39·5	62·8	53·3	57·0

(2) JOINT ACTION OF HALOGEN AND NITRIC ACID. *Schultze's Method.*—The wood is digested 10–14 days in the cold, with nitric acid of 1·10 sp. gr. to which potassium chlorate is added. The lignone is attacked jointly by chlorine and nitrogen oxides, and largely converted into derivatives soluble in the acid solution, the residues being removed by treatment with dilute ammonia. This process is unsatisfactory as a quantitative method, but is a useful illustration of the characteristics of the unsaturated lignone groups.

(3) DILUTE NITRIC ACID AT 60–80°.—The wood is digested with excess of the acid of (5–7 p.ct. HNO_3). As a result of complicated reactions comprising hydrolysis, oxidations, combination of lignone groups with lower nitrogen oxides, and destruction of these by further action of nitrous acid, a pure cellulose is finally obtained. The chemistry of the process is fully dealt with in a paper previously cited.*

Industrial Processes.—The above methods are not employed on the industrial scale, chiefly because the reagents are too costly. The manufacturers' methods of obtaining a cellulose pulp from wood all consist of hydrolytic treatment at high temperatures, of which the underlying principles will appear from the following considerations.

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* Berl. Ber., 1895, 922.

(1) ACTION OF WATER AND DILUTE ACIDS.—The action of water at elevated temperatures brings about a partial hydrolysis, but the conversion into soluble products rapidly reaches a limit determined by the opposing tendency to further condensation of the constituent groups of the lignocellulose. This is aided by the strongly acid character of the dissolved products. The results are very similar, in fact, to those obtained with the dilute mineral acids (HCl, H_2SO_4). These actions have recently been exhaustively studied by Simonsen, who has revived the idea of employing waste wood (sawdust, etc.) treated in this way as a source of fermentable sugars. By this process, the yield of 'sugar' amounts to 17–24 p.ct. of the wood, of which three-fourths yields to yeast fermentation. The yield of alcohol is 6–7 litres (absolute) per 100 kilos of wood.*

(2) ACTION OF ALKALIS.—Since the woods tend to break down under hydrolytic treatment with production of acid bodies, it is obvious that in the presence of alkalis, the limit of hydrolysis will be much extended. In fact, by employing the alkaline hydrates the decomposition proceeds to a virtual isolation of cellulose (in the form of the ultimate wood cells), the non-cellulose or lignone being almost entirely converted into soluble products.

The conditions of the 'soda process' of wood boiling are, a digestion of 7–10 hours at 90–110 lbs. steam pressure with a lye of 11–15° B.

The 'Sulphate' Process is only a variation of the above, sulphate of soda being used as the chief source of the alkali, being reduced to sulphide in the after-process of evaporating and ingiting with the organic matters, dissolved from the wood (in a previous digestion.)

(3) SULPHUROUS ACID AND BISULPHITES.—We have already seen that certain acid treatments enable us to entirely decompose the lignocellulose with isolation of cellulose—these depending upon an entire destruction of the lignone groups,

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* See E. Simonsen, Ztschr. f. Angew. Chem. 1898 [42] 962–966; [44] 1007–1012.

i.e. to products of very low molecular weights. The ketonic character of the lignone groups exposes them, on the other hand, to a selective attack by sulphurous acid. In the presence of this acid condensation of hydrolysed ketones is prevented, and under suitable conditions, which were determined as an industrial process by Raoul Pictet, this acid entirely resolves the lignocellulose into insoluble cellulose and soluble derivations of the non-celluloses, differing but little in chemical condition from that in which they occur in the original wood. This decomposition takes place at 80–110° with solutions of the acid containing 5–7 p.ct. SO_2.

But this process has ceded in industrial importance to those in which the bisulphites of the alkaline earth-metals are used as the decomposing agent. In these processes the wood, after suitable mechanical preparation, is digested for many hours at elevated temperatures with solutionsof calcium or magnesium bisulphite. In such a process it is easy to see that the hydrolysis and solution of the lignone constituents of the wood is due (1) to the action of the 'free' sulphurous (2) to the tendency of aldehydic and ketonic CO-groups to combine with bisulphites, as formulated below:

$$K \cdot HCO + MH \cdot SO_3 = H_2O + K \cdot HC(OH)MSO_3;$$

and (3) to a development of the latter reaction in cases where (as in the lignone groups) the carbonyls are combined with unsaturated residues. To take as an illustration an aromatic aldehyde of known constitution, cinnamic aldehyde, $C_6H_5 \cdot CH : CH \cdot CHO$, which forms with sodium bisulphite, first the additive compound $C_9H_8O \cdot NaHSO_3$, which on heating with the bisulphite undergoes a change to the *sulphonic acid*, $C_6H_5 \cdot CH_2 \cdot CH(SO_3Na) \cdot COH$.

From an exhaustive investigation of the soluble by-products of the process the following points have been established: that the lignone groups are dissolved with very slight constitutional change; that in solution they have the characters of sulphonated derivatives; that, however separated into fractions, these all have an identical composition, viz. that represented by the formula $C_{24}H_{23}(OCH_3)_2O_7 \cdot SO_3H$, again showing that the lignone constituents though complex are definite and homogeneous compounds; that the sulphonated derivatives still contain $CH = CH$ groups and yield brominated products of formula $C_{24}H_{22}(OCH_3)_2Br_4SO_9$.

(4) NEUTRAL SULPHITES.—It may be mentioned as of theoretical interest that solutions of the normal alkaline sulphites also determine a complete resolution of the wood into cellulose (insoluble) and lignone (groups); but owing to the feeble hydrolysing action of these salts, the reactions require higher temperatures. They partake of the characters of both the acid (bisulphite) and alkali processes, differing from the latter by minimising the secondary changes of the dissolved products.

In the table on the following page a general view of these processes is given, with names of the inventors and dates from which 'public knowledge' of the processes may be considered as beginning.

Pecto-Celluloses.—This second group of the compound celluloses will require very brief treatment—for the reason that they are not employed *as such* as paper-making materials.

The *pectic group* of plant compounds are a group of gelatinisable 'carbohydrates' widely distributed in the less permanent of vegetable structures. The general relationships of the group as determined by the earlier observers are these: *Pectose*, the insoluble mother-substance of the group, occurs in mixture or union with the cellulose of the parenchyma of fleshy fruits and roots, e.g. apples, pears, turnips, etc. This is hydrolysed by boiling dilute acids or alkalis, or by a ferment enzyme (pectase) secreted in the tissue, to *pectin* ($C_{32}H_{48}O_{32}$, Frémy), the solutions of which readily gelatinise. By continued hydrolysis (boiling water) this is further modified to parapectin, and by alkalis to metapectin and parapectic acid and pectic acid ($C_{32}H_{44}O_{30}$, Frémy; $C_{12}H_{16}O_{11}$, Regnault; $C_{12}H_{16}O_{10}$, Mulder; $C_{14}H_{22}O_{14}$, Chodnew).

The final product of hydrolysis is metapectic acid. To this acid Frémy assigned the formula $C_8H_{14}O_9$. Later investi-

VIEW OF THE CHEMICAL PROCESSES FOR DISINTEGRATING WOOD.

Aqueous Alkalis.		*Water.*		*Aqueous Acids.*	
Hydrolysis, aided by alkali directly, also indirectly by combination with products of resolution.	Watt and Burgess, 1853, Houghton, 1857.	Hydrolysis, aided by acids formed from the wood.	Fry, 1867.	(*a*) Oxidising and hydrolytic—	
		Limit of action determined by reversal of hydrolysis, i.e. dehydration aided by oxidation.		Nitric acid.	Coupier and Mellier, 1852. Barre and Blondel, 1861.
				Nitro-hydrochloric.	Orioli, 1865.
				(*b*) Simply hydrolytic—	
				Hydrochloric acid.	Bachet and Machard, 1864.
				(*c*) Reducing and hydrolytic—	
				Sulphurous acid.	Tilghmann, 1866. Pictet, 1882.
Solutions of Alkaline Sulphides.		*Water, together with neutral Sulphites.*		*Bisulphites.*	
Hydrolysis, aided by alkaline bases directly and indirectly by combination with products. Reversal of hydrolysis lessened by presence of reducing agent.	Jullion, 1855. Blitz, 1883. Dahl, 1884	Simple hydrolysis— Products removed from sphere of action by combination with base and sulphite.	Cross, 1880.	Hydrolysis, aided primarily by sulphurous acid, and secondarily by combination of products with bisulphites, also by prevention of oxidation.	Tilghmann, 1866. Mitscherlich, 1874. Ekman, 1881. Francke, 1881. Graham, 1882.
		Oxidation prevented by presence of sulphite.			

gations have established its general identity with arabic acid —a complex acid which is the main constituent of gum-arabic. Gum-arabic yields, on graduated hydrolysis, a complex of glucoses (galactose, arabinose) and a series of arabinosic acids, e.g. $C_{23}H_{38}O_{22}$, and compounds differing from this by $+ C_6H_{10}O_5$. It appears, therefore, generally, that the pectic group are compounds of carbohydrates of varied constitution with acid groups of undetermined constitution, associated together to form molecular complexes, more or less homogeneous, but entirely resolved by the continued action of simple hydrolytic agencies; and the *pectocelluloses* are substances of similar character in which the carbohydrates are in part replaced by *non-hydrolysable celluloses.* The general characteristics of the *pectocelluloses* are therefore these: they are resolved by boiling with dilute alkaline solutions into *cellulose* (insoluble) and soluble derivatives of the *non-cellulose* (pectin, pectic acid, metapectic acid); they are gelatinised under the alkaline treatment; they are 'saturated compounds,' not reacting with the halogens, nor containing any groups immediately allied to the aromatic series.

It should be noted that the later researches of Tollens [*] have thrown doubt on the conclusions of Frémy and the earlier observers as to the acid character of these 'pectic' substances. Careful analysis of a wide range of 'pectins' showed that the $H_2 : O$ ratio characteristic of the carbohydrates proper, is equally characteristic of many pectins; whereas the presence of acid groups would mean a higher oxygen ratio. It may also be noted that it is difficult to distinguish the pectins proper from the hemi- or pseudo-celluloses (see p. 50).

Generally, therefore, by a pecto-cellulose we mean a compound or intimate mixture of a cellulose with colloidal carbohydrates, or their derivatives readily hydrolysed by both acids and alkalis to simpler soluble forms. Compound celluloses of this kind are enormously diversified in composition, structural character and distribution, and the group, having none of the sharp lines of differentiation and de-

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[*] Annalen, 286, 278.

marcation presented by the lignocelluloses, cannot be handled at all in the same way.

We must confine ourselves, therefore, to the one or two more definite types which have been investigated.

Flax.—Commercial flax is a mixed product. The bast fibre proper constitutes from 20–25 p.ct. of the entire stem, and is more or less imperfectly separated from the wood on the one side, and the cortical tissue-elements on the other, by the ordinary processes of retting and scutching. These residues are visible with the naked eye, but are brought into clearer evidence by means of reagents, followed by microscopic examination. Thus the *wood* is an ordinary lignocellulose, and gives the characteristic reactions; the *cortical tissue* is again distinguished from the fibre proper by reacting strongly with magenta-sulphurous acid. The presence of the cortical tissue is also marked by the large proportion of 'oil and wax' constituents present in the fibre (3–4 p.ct.). Excluding these adventitious constituents, the fibre proper is a pecto-cellulose. That the non-cellulose constituents of flax are pectic compounds was first established by Kolb.* According to his observations, the precipitate obtained on acidifying the alkaline solutions from the 'boiling' of flax goods consists of pectic acid.

The proportion of these constituents varies from 14–33 p.ct. in the different kinds of flax, the variations being in part due to the plant, i.e. to physiological habit and conditions of growth; in part to the different methods of retting the plant—and extracting the fibre. After well boiling with the dilute alkali (1–2 p.ct. NaOH) the fibre substance consists of flax cellulose, with residues of the wood (sprit), cuticular tissues, and oils and waxes associated with the latter. By exposure to chlorine (after well washing and squeezing) the wood is attacked in the usual way, and is then easily resolved by alkaline treatment. To purify the cellulose it requires to be boiled out with alcohol, and finally treated with ether-alcohol to remove the oil-wax residues. In this way flax cellulose is

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* Bull. Soc. Ind. Mulhouse, June 1868.

isolated in the laboratory in an approximately pure condition. It might appear from the outlines of this laboratory method that the bleaching of flax goods, which consists substantially in the isolation of the pure flax cellulose, is a comparatively simple process. This is not so, however. The exigencies of economical and safe treatment of textile fabrics prescribe certain narrow limits of chemical treatment; and the removal of the more resistant wood (lignocellulose) and cuticle (cuto-celluloses) under these conditions involves a reiterated round of treatments consisting of—

Alkaline hydrolysis .	Boiling in solutions of NaOH, Na_2CO_3, etc.
Oxidation . . .	Hypochlorite solutions and atmospheric oxidation (grassing).
Souring . . .	Treatment with dilute acids in the cold.

It must be remembered, however, that the problem is not the removal of the non-cellulose constituents of the fibre itself—these disappear almost entirely in the earliest alkaline treatments—but of compound celluloses of the other two main groups.

The further investigation of the pectose of flax fibre has not been prosecuted according to the methods of later years. Such investigations will, no doubt, be undertaken in due course.

FLAX CELLULOSE has been mentioned incidentally to the general treatment of the celluloses. So far no reactions have been brought to light in which it is differentiated from cotton cellulose, with perhaps one exception, viz. its lesser resistance to hydrolysis. Thus H. Müller mentions * that flax cellulose, isolated by the bromine method, lost, on boiling five times with a dilute solution of sodium carbonate (1 p.ct. Na_2CO_3), 10 p.ct. of its weight. The statements of R. Godeffroy,† that flax cellulose is distinguished from cotton cellulose by its reducing action upon silver nitrate in boiling neutral solution, are erroneous, the reaction resulting from residual impurities, which, for the reasons given, are extremely difficult to isolate.

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* Pflanzenfaser, p. 38.

† Abstracted in Journ. Soc. Chem. Ind. (1889), 575.

Flax cellulose may therefore, for the present, be regarded as chemically indistinguishable from cotton cellulose.

The oil and wax constituents of the raw fibre will be described under the group of *cuto-celluloses.*

OTHER PECTO-CELLULOSES.—As far as investigation has proceeded, it appears that pectose, or pectose-like substances, are associated with all fibrous tissues of the unlignified order. And indeed in the lignocelluloses themselves pectous substances make their appearance with increasing age. Thus the lower portions of the isolated jute bast—jute cuttings or butts —when boiled in alkaline solution yield products which cause the solution to gelatinise on cooling; and the gelatinous product is insoluble in alcohol, distinguishing it, as pectic acid, from the products of hydrolysis of the lignocellulose itself, which are dissolved, after precipitation, by alcohol. It must be remembered, however, that in the 'jute cuttings' the adhesion of the bark and cortical parenchyma to the true bast fibre is such that we are dealing with a complex tissue, and the source of the pectic acid may be in the parenchyma of the tissue and not in the bast fibre. On the other hand, it has been shown that in the spontaneous decomposition of jute, lying in the damp state, gelatinous acid bodies are formed indistinguishable from pectic acid. It would not be difficult, therefore, to account for the pectic constituents of the bast tissue towards the root end as products of degradation of the lignocellulose itself.

Reverting, however, to the non-lignified fibres such as China grass, or Ramie (Böhmeria species), and the 'nettle fibres' generally, hemp, and even raw cotton—these all contain pectic bodies associated with the cellulose, which are hydrolysed and dissolved by treatment with boiling alkalis. But these pecto-celluloses have not been sufficiently investigated *as* compound celluloses to admit of any useful classification on the basis of particular constitutional variations of their non-cellulose constituents.

The mono-cotyledonous fibre-aggregates, whether fibre-vascular bundles (Phormium, Aloe fibres, Musa, etc.) or entire plants (Esparto, Bamboo stems, Sugar Cane), are largely made up of pecto-celluloses, with a greater or less proportion of lignocelluloses. But the constitution of these non-cellulose constituents is as yet quite unknown, and we have therefore none but the general basis of classification.

In the same way also the parenchymatous tissue of fruits, fleshy roots, etc.—the typical pecto-celluloses—must be, for the present, dismissed with the bare mention.

The investigation of these substances belongs rather to the province of general carbohydrate chemistry than to the narrower cellulose group; and the problems involved are in many respects rather morphological and physiological than purely chemical.

These same considerations apply also in great measure to the mucilaginous constituents of plant tissues, though certain of these have been investigated by modern chemical methods. The relationship of these substances to cellulose is indicated (*a*) by the histology of the tissues, which shows them to be associated with the *cell wall* rather than with the cell contents; (*b*) by their empirical composition, which is approximately that of cellulose; (*c*) by their reactions with iodine, by which they are coloured variously from blue to violet, as are the hydrated modifications of cellulose.* Beyond superficial observations of reactions (iodine) and gelatinisation with water, these compound celluloses—which may conveniently be termed muco-celluloses—had been but little investigated † until the systematic work of Kirchner and Tollens, and Gans and Tollens, ‡ upon the mucilages and gums.

Cuto-celluloses [*Adipo-celluloses*].—The plant represents, in the one view, an assemblage of synthetical operations carried on within a space enclosed and protected from the destructive influences of water and unlimited atmospheric oxygen. The protecting external tissues are those which we are about to describe as constituting the third important group of compound celluloses. These tissues contain, in

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* Sachsse, Farbstoffe, etc., p. 161.

† Sachsse, *loc. cit.*

‡ Annalen, 175, 205; 249, 245.

admixture with the tissue-substance, a variety of oily and waxy products (easily removed by mechanical solvents), the presence of which adds very considerably to the water-resisting property of the tissue. It will be seen as we proceed, however, that the tissue-substance, after being entirely freed from these adventitious constituents or oily excreta, yields a large additional quantity of such products when decomposed by 'artificial' processes of oxidation and saponification. By this and by its empirical composition (*infra*) the tissue-substance will be seen to contain 'residues' of high carbon percentage and molecular weight, and closely allied in chemical structure to the oil and wax compounds found in the 'free' state in the tissue as it occurs in the plant. These groups are associated in combination in the tissue with cellulose residues, and hence the description of such complexes as adipo-celluloses.

There are two main types of these compound-celluloses, viz. cork and the cuticular tissues of leaves, stems, etc.

CORK in its ordinary form is a complex mixture containing not only oils and waxes, but tannins, lignocelluloses, and nitrogenous residues. The following are the results of elementary analysis: (*a*) of cork purified by exhaustive treatment with ether, alcohol and water; (*b*) of cork (*Quercus suber*) without purification; (*c*) of the cork tissue of the cuticle of the potato (tuber) purified by exhaustion with alcohol:—

	(*a*)	(*b*)	(*c*)
C	67·8	65·7	62·3
H	8·7	8·3	7·1
O	21·2	24·5	27·6
N	2·3	1·5	3·0

The analyses are calculated on the ash-free substance.*

These investigators succeeded in isolating cellulose from cork, but by complicated and drastic methods of treatment, such as would break down the greater proportion of the cellulose into soluble derivatives. These treatments were:

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* Döpping, Annalen, 45, 286; Mitscherlich, Annalen, 75, 305.

(1) drastic oxidation with nitric acid; (2) alternate treatments with boiling dilute hydrochloric acid and 10 p.ct. solution of potassium hydrate. The proportion thus isolated amounted to 2–3 p.ct. only.

The authors, on the other hand, have observed that the non-cellulose of cork is entirely converted into soluble derivatives by the process of digestion at high temperatures with solutions of the alkaline sulphites, as described, p. 66. In this way a residue is obtained preserving the form (i.e. cellular structure) of the original cork, and amounting to 9–12 p.ct.

The details of a particular experiment were as follows: 10·995 grms. cork, 20 grms. $Na_2SO_3.7H_2O$, 2 grms. Na_2CO_3, dissolved in 500 c.c. water. Digested 3 hours at 75 lbs., and 4 hours at 125 lbs. pressure. Residue bleached with sodium hypochlorite solution. Yield of cellulose, 1·34 grms.; 12·1 p.ct.

These relationships have been more definitely made out by Frémy, in his investigations of the closely allied compound which constitutes the epidermal or cuticular tissue of the leaves, stems, etc., of Phanerograms. As the characteristic constituent of cork is termed suberin, so Frémy terms this cuticular tissue-substance cutin or cutose. To prepare this substance, cuticular tissue ('peel') of the apple, e.g., is treated with boiling dilute acids, followed by digestion with the cuprammonium reagent (p. 9); then again with boiling acid and dilute alkali (KOH); finally the residue is treated with alcohol and ether. In this way a nitrogen-free residue is obtained having the empirical composition:—

C	73·66	p.ct.
H	11·37	„
O	14·97	„

Not only by these results, but by the study of the proximate resolutions of this substance, it is shown to have the closest relationships to the carbon compounds of the 'wax' class.*

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* Compt. Rend., 48, 667.

In a later investigation of the products of saponification of this substance, Frémy worked upon a raw material similarly prepared, but having the composition C 68·3, H 8·9, O 22·8. This compound is termed *cutose*, in substitution for cutin. Cutose is slowly attacked by boiling alkaline solutions; a product is dissolved, *of the same empirical composition* as cutose,* but of a fatty nature. It is precipitated on acidifying the solution; the precipitate is soluble in ether-alcohol, and when isolated is found to melt below 100°. Under more drastic treatment with alkaline solutions the dissolved products are found to be a mixture. Precipitated by acids and treated with boiling alcohol, the mixture dissolves; on cooling, the solution deposits an acid (m.p. 85°) in yellow-coloured flocks, which after fusion form a brownish translucent friable mass. This is a compound of *stearocutic acid* and *oleocutic acid* (*infra*), into which it is resolved by further treatment with alkali. The alcoholic filtrate from the solid acid when evaporated gives a viscous residue, of an acid body, *oleocutic acid.*

By the further action of very concentrated potash solution in the yellow acid, stearocutic acid is formed. The potash salt of this acid is white and translucent, insoluble in water and cold alcohol, soluble in boilng alcohol. The free acid (m.p. 76°) is also insoluble in cold alcohol, slightly only on boiling, but dissolves in benzene and in acetic acid on warming. The acid also dissolves freely in alcohol in presence of oleocutic acid. A similar result is seen with the potassium salt, which, though insoluble in water, dissolves in an aqueous solution of potassium oleocutate.

The composition of these two acids is as under:—

Stearocutic Acid.

C	75·00
H	10·71
O	14·28

which is expressed by the formula $C_{28}H_{48}O_{24}$. This formula is confirmed by the analysis of the salts of the acid.

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* Comp. Lignocelluloses, p. 57.

Olecoutic Acid.

C	66·66
H	7 91
O	25·43

expressed by the formula $C_{14}H_{20}O_4$.

Cutose is regarded by Frémy as a complex of these two compounds, in the proportion of 1 mol. stearocutic acid: 5 mols. oleocutic acid. These acids undergo alteration on heating at 100° in presence of water, passing into insoluble modifications of higher melting point. The original molecular condition, however, is restored on heating with alkaline solutions.

Frémy also made observations upon suberin (or suberose), which yielded similar products of saponification. He therefore concluded that the two products are substantially identical. The products of oxidation by nitric acid are also indistinguishable, viz. chiefly suberic and succinic acids.

These results suggest, from the purely chemical standpoint, that the cellulose of the tissue and the waxy products of excretion stand to one another in a genetic relationship, and the cutose or suberose occupies an intermediate position. The question of a direct conversion of cellulose into wax taking place in these cuticular tissues was definitely raised and discussed by De Bary in his investigations of this group of plant constituents.* It appears from these researches that wax-alcohols are certainly not contained in the cell-sap or protoplasm, and that their origin must be in the cuticular tissues themselves; but the parent substance may be either cellulose, or some compound built up with it in the ordinary course of elaboration. This question is left for the present undetermined. It should be borne in mind, on the other hand, that we have a great number of direct observations upon the physiological equivalence of the carbohydrates and the fats, both in the animal and vegetable worlds; and although the mechanism of the transformation of the one

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* Bot. Ztg. 1871.

into the other group of compounds remains unelucidated, it is after all not more difficult to imagine than the condensation to furfural. It is, however, not the purpose of this treatise to carry discussion into purely speculative regions; and it is sufficient to state the conclusion that there is ample ground for adopting as a working hypothesis that carbohydrates, or possibly cellulose, are transformed into cutose or suberose, and these, again, into free waxy bodies of lower molecular weight, the whole process representing the change known as cuticularisation or suberisation.

the structure of the fibres to the qualities of the papers which they compose. Other equally important practical bearings will be seen to attach to the microscopic study of our fibrous raw materials, and to the consideration of this branch of the subject we now ask the careful attention of the student.

Microscopical Examination.—Under the head of 'Microscopic Features' we must include everything which has to do with the structure of the vegetable fibres, as well as their organisation and distribution in the plant. In the analysis of 'organised' structures we employ the two methods (1) of *dissection;* (2) *examination* by means of the microscope; in other words, we first isolate the part under investigation by a mechanical process, and then proceed to the optical resolution or analysis of the part. Having by analysis acquired a knowledge of the *parts*, we study their mutual relations in the structure they compose—we integrate our knowledge, so to speak—by means of sections of the structure, cut so as to preserve the cohesion of the parts in section, and yet in so fine a film as to appear under the microscope to be virtually a plane surface. These points are illustrated in the drawings given.

It is impossible for us to deal specially with the subject of the microscope and its manipulation. The microscope, as a revealer of natural wonders, is one thing; as an instrument of scientific discovery, quite another. For the latter, the student must train himself by systematic work, and should especially concentrate his attention upon some *one* branch of natural history, however restricted.

We shall assume, in our treatment of the subject, a knowledge of the microscope as an instrument of research, such as can be easily acquired in a few weeks of work under the guidance of a teacher or of one of the excellent manuals which now abound. We also assume a certain acquaintance with the elements of vegetable physiology, which it will be seen is necessary for a full grasp of the subject. Such an acquaintance, also, may be easily acquired, under direction, in a few weeks of work.

We have before alluded to the difference presented by mono- and di-cotyledonous stems in regard to the distribution of their fibrous constituents. In illustration of this, we may cite Figs. 2, 3, which represent (2) a section of the aloe, (3) a section of the jute plant. The available fibres are in

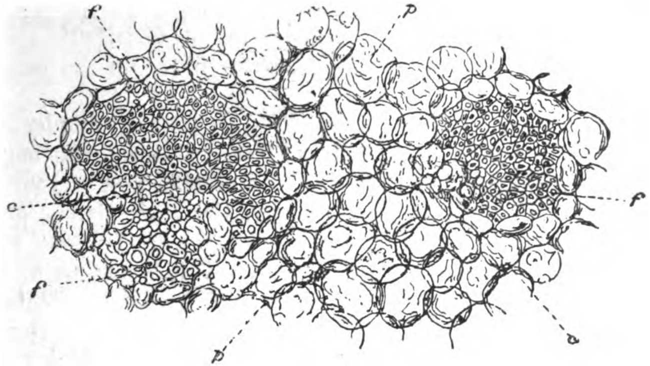

FIG. 2.

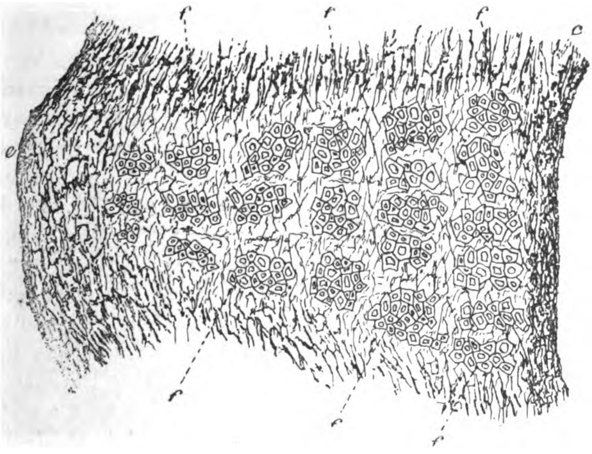

FIG. 3.

(2) the fibro-vascular bundles (*f*), which are irregularly distributed throughout the main mass of cellular tissue, and in (3) the bast fibres (*f*), which constitute a definite and separate tissue. We have already alluded to the practical consequences of this typical difference of distribution, in regard to processes of separating these fibres on the large scale.

This process we have explained is necessarily simpler in the case of a fibrous *tissue*, definitely localised; and this may be demonstrated by a superficial examination of a young branch of an exogen. As we know, the bark tissues are easily stripped from the underlying wood. If now we work up the former in a mortar, with a little water, we soon perceive the separation of the compound tissue into cellular matter, on the one hand, and *fibres*, the latter being more or less long and silky, according to the plant from which isolated. They vary in length from one millimetre to several centimetres, and are aggregated together in the plant in such a way as to constitute bundles, often of very considerable length; the general arrangement being comparable with that of the tiles in the roof of a house. It is important to distinguish the fibre-bundles from the elementary or normal *fibres*, and to this end they are designated by the term *filament*. Bast *fibres* are flexible and fusiform, terminating gradually in a point at either end, as represented in Fig. 4; bast *filaments*, built up of these fibres, containing often as many as twelve in the bundle, are usually cylindrical, but exhibit the widest differences in regard to the aggregation in degree as well as number and dimensions of their constituents. It is obvious that while the spinner has to do with these *filaments*, the paper-maker works up the ultimate fibre constituents or *fibres*. It is also an obvious corollary from this distinction that a fibrous material which from 'weakness' is unavailable for textile application, may yet be perfectly 'strong' from the paper-maker's point of view; in other words, the individual fibres may be strong, but have little cohesion in the filaments. As we proceed, the student will see more and more the practical bearings of this branch of the study, and will perceive the inferences to be drawn from the investigation of minute relationships to manufacturing processes and their products.

We shall say but little as to the necessary equipment. (1) A dissecting microscope, for dissecting under a lens, magnifying the object to 40 or 50 diameters. (2) an ordinary student's microscope, with lenses for magnifying to 100 and 300 diameters. This is adequate to the work, though, of course, it may be an advantage in certain cases to be provided with higher powers. (3) A glass slide, carrying an engraved scale of centimetres and millimetres for measuring the lengths of objects, and a micrometer, divided into $\frac{1}{10}$ mm. for measuring diameters. It is also important to be able to determine the degree of enlargement under any particular combination of lenses, and for this purpose to possess a micrometer eye-piece, with a millimetre scale divided into hundredths. (4) An effective microtome, and the usual mounting accessories.

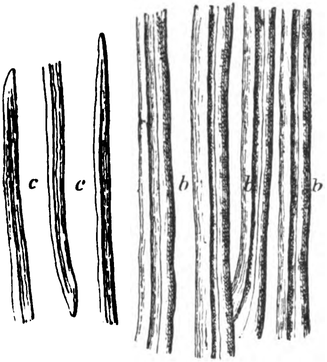

FIG. 4.

A very important feature in the diagnosis of fibres, more especially in regard to the composition of the fibre-substances, is the effect produced by treatment with various reagents. Certain of these reactions we have already indicated. We shall now give the details of composition of the several solutions which will be required.

Mounting Solutions.—In preparing objects for observation under the microscope, they may be mounted in water, or mixtures of glycerin with water. In examining fibres or fibrous structures under chemical treatment, they may be mounted in the solutions in which they are undergoing treatment. In mounting transparent objects it is sometimes required to employ a solution of the same refractive power as the substance itself. For this purpose, pure or diluted glycerin or a syrupy solution of calcium chloride may be employed; it is expedient to mix with either reagent a small proportion of acetic acid. When the objects are to be stained or otherwise treated while under observation, they must be first mounted in a neutral medium, e.g. water or dilute glycerin. The designation 'neutral' has reference to the fact that these reagents are without sensible action on the fibres.

IODINE SOLUTION.—We have previously described the preparation of a solution giving the characteristic blue reaction with cellulose directly. It is, however, often preferable to bring about this coloration in another way, and the following are the solutions employed:—1 gramme of potassium iodide is dissolved in 100 c.c. water, and the solution is saturated with iodine; it is preserved in stoppered bottles, containing a few fragments of the element, so as to keep up the saturation of the solution.

The accessory solution, dilute sulphuric acid, which is employed to determine the reaction between the cellulose and the iodine, is prepared as follows:—2 volumes of concentrated glycerine are mixed with 1 volume water, and to the mixture an equal volume of oil of vitriol (1·78 sp. gr.), is slowly added, so as to prevent as far as possible a rise of temperature. The effect of the glycerin is very remarkable in preventing the distortion of the objects under the action of the acid, which in other respects remains uninfluenced.

By way of verification of this iodine test, which is somewhat capricious, it is advisable to test the reagents with a standard substance. The best for the purpose is a linen yarn which has been *partially* bleached. Under the action of the reagents the fibres composing this yarn (which must, of course, be suitably 'teazed out' for mounting) are coloured a light blue, the centre, however, showing a yellow line, marking the distribution in the interior canal of a non-cellulose fibre constituent. Should these effects not appear, it may be concluded that the acid requires to be strengthened. On the other hand, too great a concentration is equally to be avoided; it is evidenced by causing a *distortion* of the fibre, easily recognised by comparison with the fibre mounted in a neutral medium.

CHLORINE WATER.—One of the most characteristic reactions of lignose, or lignified cellulose, is that of combining with chlorine. The reaction of the chlorinated derivatives with sodium sulphite solution is an important feature in the microscopic diagnosis of lignified fibres and cells. The reagent is prepared by dissolving chlorine to saturation in water. The sodium sulphite solution is prepared by dissolving the crystallised salt in 20 parts distilled water.

ANILINE SULPHATE SOLUTION.—With this reagent lignose gives a characteristic deep yellow coloration. A convenient strength is a 2 p.ct. solution of the salt. The colour is more quickly developed if the reagent is acidified; a few drops of sulphuric acid should therefore be added.

PHLOROGLUCOL REAGENT.—The crystalline phenol is dissolved to saturation in the cold in hydrochloric acid of 1·06 sp. gr. Lignified fibres and cells are stained a full magenta red by the reagent.

DIMETHYL-PARAPHENYLENE DIAMINE.—Solutions of this base are unstable, but the addition of acetic acid confers a more permanent character. The deep red coloration produced with the lignocelluloses is useful in micro-chemical investigations.

Solutions of the Aniline Colours.—Some of these are of importance in enabling the microscopist to differentiate plant tissues. The 'affinities' of the fibre-substances for these are very various in kind and intensity. The phenomena of staining cannot be adequately treated in our histological scheme, which is necessarily very restricted. We therefore merely mention the more important colours which are used in staining, viz., magenta, methylene blue, eosine, diphenylamine blue. A convenient strength is a solution of 1 in 2000. (See also p. 202.)

The above-mentioned reagents are a sufficient equipment for all ordinary work. Their employment presents no difficulties, and therefore no detailed descriptions are necessary. In more advanced investigations, the student will make his own selection of special reagents according also to the composition of the colouring matter. In following up this subject, he will require to consult works on vegetable histology.

Preparation of the Objects.—The necessary preliminary to the examination of the fibres themselves is their isolation. This is accomplished either by means of the dissecting microscope, or more roughly, according to circumstances. Having obtained the filaments, they are boiled in a 10 p.ct. solution of sodium carbonate, or a 2 p.ct. solution of caustic soda (NaOH), until sufficiently softened to yield easily to the 'teazing' needles. In certain cases the boiling must be supplemented by trituration in a mortar; this, or some similar operation, is especially necessary when the fibres are embedded in a mass of cellular tissue (parenchyma), e.g. in the fibro-vascular bundles of monocotyledons.

Sections of the filaments are prepared by cutting in a microtome, the filaments being previously agglutinated into a stiff bundle by means of any of the usual stiffening solutions, and, after drying, embedded in wax in the usual way. Sections of fresh stems and tissues are cut with a 'section' razor.

As an agglomerating agent, solutions of the cellulose sulphocarbonate, containing 2–3 p.ct. of dissolved cellulose, are especially to be recommended. In place of wax, a strong alcoholic solution of ordinary yellow soap is used with advantage as a medium for embedding. The specimens are introduced into the hot solution, which sets on cooling to a firm sectile mass.

Having prepared the objects, their examination under the microscope necessarily divides itself into (1) the determination of external features; (2) the diagnosis of chemical composition. The fibres themselves will be individually considered in regard to microscopic features.

There is one aspect of these structural features, however, which admits of more general treatment, and in respect of which we may anticipate with advantage, viz. the dimensions or simple elements of form. The importance of the determination of the length and diameter of both filaments and fibres will be readily appreciated by an inspection of the following table, in which the numbers are given for several of the more important.

A careful study of this table in relation to the application of these several fibres, will show that the correlation of the latter with these ultimate dimensions is close and essential.

These measurements of length and diameter are made in various ways. Thus, the object may be made to move across the field of vision, the extent of movement being recorded by means of a vernier attached to the stage itself. Another device is that of the micrometer eye-piece, by which a graduated scale is brought into the field of vision and is brought to bear upon any object, just as an ordinary measuring rule or tape.

A very important point in the diagnosis of a raw material, and next in order of treatment, is the degree of purity of the substance, in so far as this is related to structure. The fibres may be associated with cellular tissue, or with cellular débris, if they have undergone the retting process or other treatment for separation; or with 'encrusting and intercellular substances' in various proportions. In the latter case the

TABLE OF LENGTHS OF RAW FIBRES (FILAMENTS) AND DIMENSIONS OF CONSTITUENT CELLS AND FIBRES.

	—	Average Length of Filament.	Average Length of Fibres.	Diameter of Cells.	
				Extreme.	Normal.
		mm.	cm.	$\frac{1}{100}$ mm.	$\frac{1}{100}$ mm.
A. *Seed hairs.* Filaments composed of individual cells.	*Cottons.* *Gossypium barbadense* . . (Sea Island)	..	4·05	1·92–2·79	2·52
	Gossypium acuminatum . .	..	2·84	2·01–2·99	2·94
	Gossypium arbo reum . . .	..	2·50	2·00–3·78	2·99
	Bombax heptaphyllum .	..	2–3	1·9–2·9	..
B. *Bast-fibres.* Filaments or fibre bundles, made up of individual fibre-cells aggregated together.	*Flax.* Linum usitatissimum . .	20·140	2·0–4·0	1·2–2·5	1·6
	Hemp. Cannabis sativa .	100-300	..	1·5–2·8	1·8
	China Grass. Boehmeria nivea .	..	22·0	4·0–8·0	5·0
	Ramie. Boehmeria tenacissima . .	..	8·0	1·6	..
	Jute. Corchorus capsularis . . .	150–300	·2	1·0–2·0	1·6
	Corchorus olitorius	150–300	·2	1·6–3·2	2·0
	Paper mulberry. Brousonetia papyrifera . .	..	·7–2·1	..	3·6
	Linden bast. Tilia grandifolia	..	1·1·6	..	1·5
C. Fibro-vascular bundles.	*New Zealand Flax.* Phormium tenax .	80–110	m.m. 2·5–5·6	·8–1·9	1·3
	Aloe. Aloe perfoliata .	40–50	1 3–3·7	1·5–2·4	..
	Esparto. Stipa tenacissima	10–40	·5–1·9	·9–1·5	..

association with the fibres is usually much more intimate; they are, in fact, essential constituents of the fibre *bundles* (lignified bast-fibres, fibro-vascular bundles), whereas the former we may regard as 'foreign matter.' We may, however, distinguish between the normal 'incrustation' of the fibre-cells, and such an incrustation of the filaments as would be described as a loose adhesion of non-fibrous matter. The latter is seen in such tissues as the bast of the adansonia, and the fibro-vascular bundles of the aloes. These are points with which observation alone can familiarise the student; as experience grows he will find it increasingly easy to follow *general* distinctions, and in proportion as he uses his own faculties, so he will be able to generalise for himself. He will find this equally true of the second section of the microscopic examination, i.e. the micro-chemical diagnosis of fibres. Under this head is included the observation of the behaviour of fibres towards the various reagents above described. In addition to their microscopical employment, it is useful to note their effect on fibres in the gross, both in their natural state and after treatment with bleaching agents.

In applying the iodine reaction, attention must be paid to the following details of manipulation. Place the object (dry) upon the glass slide, moisten with a few drops of the iodine solution, cover with a glass slip, and examine under the microscope. Note the effects, which are those of the iodine alone. Then remove the iodine solution by means of blotting paper, and introduce the sulphuric acid by the method of 'irrigation.' The coloration of the cellulose (blue-violet) is immediate; it has the effect, moreover, of bringing out more clearly a number of the structural details of the fibre.

We have already treated of the resolution of the raw fibres into cellulose and non-cellulose constituents by processes which convert the latter into soluble derivatives. The student will derive much instruction from following up the attendant structural disintegration with the aid of the microscope. The chemical dissection of lignified fibres by the alternate action of bromine water and alkalis, should be studied by mounting specimens of the fibre at all stages and carefully noting all the changes which occur. The more drastic action of chlorine should also be studied by mounting the chlorinated fibre (in water) and then irrigating with the alkaline solvent (caustic alkali or sulphite) and noting, the stages in the completion of the disintegration.

CHAPTER III.

SCHEME FOR THE DIAGNOSIS AND CHEMICAL ANALYSIS OF PLANT SUBSTANCES.

IT will be convenient at this point to present to the reader a general scheme for the chemical analysis of fibrous raw materials.

We have already described various methods for the determination of cellulose in fibrous substances. This is to the paper-maker the most important constituent, and is that upon which his calculations of the value of a raw material are based. Not only, however, is it of the greatest importance for him to be able accurately to determine the *amount* of cellulose, but it is necessary to be able to form some idea of the nature of the cellulose and also the ease with which it can be obtained from the fibre. This latter point can only be properly established by direct trial of the fibre under the conditions existing in the factory. A practical assay of a raw material for 'paper-making cellulose' is best carried out in a model digester capable of treating from 500 to 1000 grammes of raw material. In such an apparatus a digestion with alkaline lye, or with bisulphite liquor can be carried out at elevated temperatures exactly as on the large scale.

Where such small digester is not available, the fibrous material may be enclosed in a bag of resistant material, sufficiently open to allow for penetration of liquid, and close enough to prevent escape of fibre. The bag is placed in the ordinary boilers in the mill, as charged with material for 'boiling'; at the conclusion of the 'boil' it is removed to the laboratory and worked up by washing, etc., for the complete isolation of the fibre.

To complete the purification of the cellulose, where this is necessary, it is bleached with a solution of bleaching powder. The experiment is made a quantitative measure of the amount of bleaching chlorine required, by taking a measured volume of a solution of known strength, in calculated excess, and, when the bleaching of the fibre is completed, estimating the 'residual chlorine' by an observation in a known fraction of the liquid with which the bleached pulp is in contact.

In the manipulation of fibrous materials, filters of cotton cloth will be found most suitable. The qualities most suitable are the ordinary printers' calico (bleached), nainsook, and muslins of varying fineness according to the nature of the material. These filters may be supported in glass funnels, and after collecting and washing the fibrous product, the mass may be lightly squeezed to retain not more than its own weight of water. After squeezing it is easily detached from the cloth.

By the operations of isolating the cellulose, preceded or accompanied by microscopic observations such as we have described, a fair general account will have been given of any fibrous material. But, to complete the investigation, a scheme of determination should be carried out as shown on the next page.

These determinations are the practical application of the principles elucidated in Chapter I. It only remains now, therefore, to add certain notes of practical points to be observed in the experimental study of raw materials.

1. MOISTURE.—The mere operation of drying at 100° determines molecular changes in such compounds as the lignocelluloses—changes which affect the subsequent action of reagents. It is necessary, therefore, to weigh separate portions for the particular experiments in the air-dry condition, and calculate the dry contents from the data of the specimen weighed after drying at 100°.

FAT, WAX AND RESIN.—These constituents are estimated as an aggregate extract obtained by boiling out with hydrocarbon solvents, or with ether-alcohol.

Separate portion taken for each determination. Results calculated in percentage of dry substance.	Moisture . .	. Hydroscopic water, or water of condition. Loss in drying at 100°.
	Ash . .	. Total residue left on ignition.
	Hydrolysis (*a*)	. Loss of weight on boiling 5 minutes in 1 p.ct. solution of caustic soda.
	„ (*b*)	. Loss of weight on continuing to boil 1 hour.
	Cellulose . .	. Isolation and estimation as previously described.
	Mercerising .	. Loss of weight on treating 1 hour with strong solution of caustic soda, 15-25 p.ct. NaOH.
	Nitration . .	. Weight of nitrated product obtained by treatment with mixture of equal volumes of nitric and sulphuric acids 1 hour in the cold.
	Acid purification .	Loss of weight after boiling with 20 p.ct. acetic acid and washing with water and alcohol.
	Carbon percentage.	Determined by combustion.

2. ASH.—The specimen weighed after drying at 100° may then be burned for the determination of ash. The ash in isolated fibres is low, viz. 1–2 p.ct.; in fibre aggregates it is often high—thus, in esparto and straw, from 3–6 p.ct.—and should be taken into account in calculations of yields or loss of weight. In such cases, after weighing the product of any given reaction the specimen, or a portion of it, should be burnt and the ash determined. The ash-free product is calculated in terms of the original substance, also taken ash-free.

The ash constituents are (1) those of the normal fibre, and (2) in certain cases, adventitious mineral matter. These are easily distinguished and separately estimated.

3. ALKALINE HYDROLYSIS.—This is obviously the first stage towards the isolation of cellulose. When the numbers obtained for the short period (*a*) and for the long digestion (*b*) show a marked difference, it is an obvious general indication of low paper-making quality.

4. CELLULOSE.—Having isolated a white residue from a raw fibrous material, it may be weighed and then further

investigated. An estimation of furfural will establish its position in the classification of the celluloses.* For practical purposes it is sufficient to establish the degree of resistance of the cellulose to further alkaline hydrolysis and to oxidation by alkaline cupric oxide (Fehling's solution).

5. MERCERISING.—The effect of the action of caustic soda as measured by loss of weight, and also changes in appearance and structure, may be usefully observed on the isolated celluloses, and in certain cases upon the raw fibrous materials. The pecto-celluloses are considerably gelatinised by the treatment, the fibres often undergoing agglomeration, and drying to a harsh wiry condition. The lignocelluloses are affected in the contrary direction. The cuto-celluloses are not all attacked. From all the above treatments the product should be treated with dilute acids by immersion in the cold, and copiously washed before drying. The drying is much accelerated by treatment with alcohol.

6. 'NITRATION,' or conversion into nitric esters, affords useful information; but judgment must be exercised as to the applicability of the treatment to the raw material, to the partial purified products (alkaline hydrolysis), or to the isolated cellulose. It is a general measure of the proportion of reactive alcoholic OH groups, and also of resistance to oxidation.

7. ACID PURIFICATION removes basic mineral matter, often present in some quantity in raw materials of the pecto-cellulose class. It may sometimes be required to attack and remove more resistant mineral constituents such as silica and silicates. In this case the material may be digested with a mixture of hydrofluoric and hydrochloric acids in vessels suitably resistant to the action of these acids. The treatment is followed by copious washing.

8. CARBON PERCENTAGE.—This is only necessary in certain investigations. The value of the constant will be recognised from the fact that it varies considerably for the different groups of compound celluloses. The most convenient method

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* For which, see *ante*, pp. 45–52.

is that of combustion with chromic acid after solution in sulphuric acid.*

In addition to the above, other determinations may in certain cases be usefully carried out. Thus an observation of the loss of weight in boiling with dilute acid (1 p.ct. HCl, or H_2SO_4) supplies an approximate measure of the more easily hydrolysed carbohydrates, e.g. hemi-celluloses. The ferric ferricyanide reaction especially characteristic of the lignocelluloses, may be quantitatively carried out, the fibre being prepared by a weak alkaline treatment, washed and placed in a cold solution of the reagent at standard strength, prepared by mixing equal volumes of solutions of ferric chloride containing 16·2 grms. $FeCl_3$ per litre, and of potassium ferricyanide containing 33 grms. K_3FeCy_6 per litre. The gain in weight due to the deposit of the Prussian blue is a measure of the lignone groups. †

Investigations of the more extended character will be found indispensable in the examination of raw materials which are 'new,' or as yet untried as sources of paper-making fibres. But for what we may call standard materials, it is obvious that the practically important characteristics are those which relate to cellulose—quantity and quality—and the degree of resistance of the cellulose to alkaline hydrolysis and oxidation.

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* The details of the method will be found described in Journ. Chem. Soc. 53–889.

† See 'Cellulose,' p. 124; and H. C. Sherman, Journ. Amer. Chem. Soc. 1897, 19, 291–310.

CHAPTER IV.

AN ACCOUNT OF THE CHEMICAL AND PHYSICAL CHARACTERISTICS OF THE PRINCIPAL RAW MATERIALS.

THIS chapter contains the results obtained from an investigation of the different plant fibres by the methods indicated in the two previous chapters.

In the following table the fibres are classified according to the reactions which they give with iodine solution.

CLASSIFICATION OF PLANT FIBRES ACCORDING TO THEIR COLOUR REACTION WITH IODINE SOLUTION (VÉTILLART).

	A. Seed Hairs.	B. Dicotyledonous Bast Fibres.	C. Monocotyledonous Fibres.
Blue reaction	Cotton.	Linen. Hemp. China grass. Paper mulberry. Sunn.	Straw. Esparto. Pine apple.
Yellow reaction		Jute. Hibiscus.	New Zealand flax. Yucca. Aloe. Manilla hemp.

CLASS A.

Cotton.—Genus *Gossypium.* Order *Malvaceæ.* Seed hairs, consisting of ultimate fibres. Length, 2·0–4·0 cm., diameter, 0·012–0·037 mm. Mean ratio, 1250. Illustrated in Fig. 5: *a*, sections; *b*, longitudinal views; *c*, ends; mag. 300.

Microscopic features. Fibre simple, opaque, flattened, always more or less twisted upon itself, side wall membranous, showing striæ.

Sections: Simple, oval, irregular, central cavity often containing granules.

Micro-chemical reaction: Blue with iodine solution.

General chemical characteristic: Pure cellulose basis with slight admixture of colouring matters, etc.

COMPOSITION OF RAW FIBRE.

	Church.	Müller.
Cellulose	91·15	91·35
Fat	0·51	0·40
Aqueous extract (containing nitrogenous substances)	0·67	0·50
Water	7·56	7·00
Ash	0·11	0·12
Cuticular substance (by difference)	..	0·63

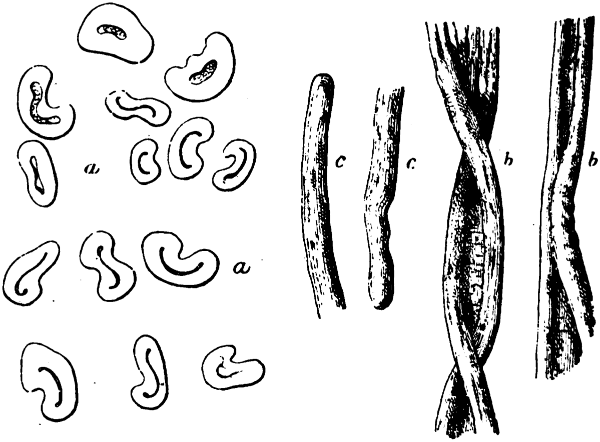

FIG. 5.

E. Schunck, in his investigation of cotton bleaching,[*] finds that in boiling with sodium carbonate solution the fibre loses 5 per cent. in weight. Some portion of the dissolved substances is precipitated on acidifying and is found to contain a wax, brown resinous and colouring matters, and pectic acid.

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[*] Chem. News, 17, p. 11.

Forms in which employed.—Fibrous refuse from the decortication of the seeds; spinning waste, threads, rags, new and old.

Class B.

Flax.—Genus *Linum*. Order *Linaceæ*. Bast-fibre and filaments. Lengths of fibres, 25–30 mm.; diameter, 0·02 mm., ratio, 1200. Illustrated in Fig. 6: *a*, sections of the fibres, isolated and in groups; *b*, the fibres viewed longitudinally, one showing the creases produced by repeated bending; *c*, ends; *a′*, sections of fibres situated near the butt of the plant; mag. 300.

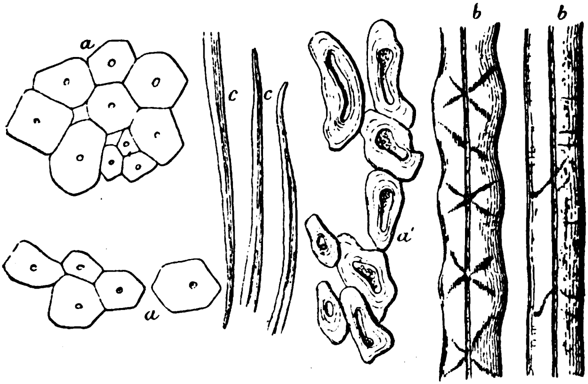

Fig. 6.

Microscopic features.—Fibres transparent, regular, with tapered ends, side walls thick, consequently central canal small, smooth externally, sometimes slightly striated. Filaments easily split up into fibres.

Sections.—Polygonal, regular, angles more or less acute, lumen represented by point; slight indications of concentric arrangement of fibre-substance.

Micro-chemical reaction.—Blue with iodine solution.

General chemical characteristic.—Pecto-cellulose with residues of wood (ligno-cellulose) and cuticle (cuto-cellulose).

Composition of raw fibre. This varies with the different species, and is doubtless also influenced by variations in the processes of retting. The following are the analyses of two samples of Belgian flax (heckled):—

	Müller,	
Cellulose	81·99	70·75
Fat and wax	2·37	2·34
Aqueous extract	3·62	5·94
Pectous substances	2·72	9·29
Water	8·60	10·56
Ash	0·70	1·32

The chemistry of the flax fibre has been investigated by Kolb, F. Hodges and the authors.[*]

Forms in which employed.—Scutching refuse, spinning waste, threads, rags (new and old).

Hemp.—*Cannabis sativa.* Order *Cannabinaceæ.* Bast-fibres: length, 22 mm.; diameter, 0·022 mm.; ratio, 1000. Illustrated in Fig. 7: *a*, *a'*, sections of groups of fibres of the first and second zone respectively; *b*, fibres seen longitudinally; *c*, ends; mag. 300.

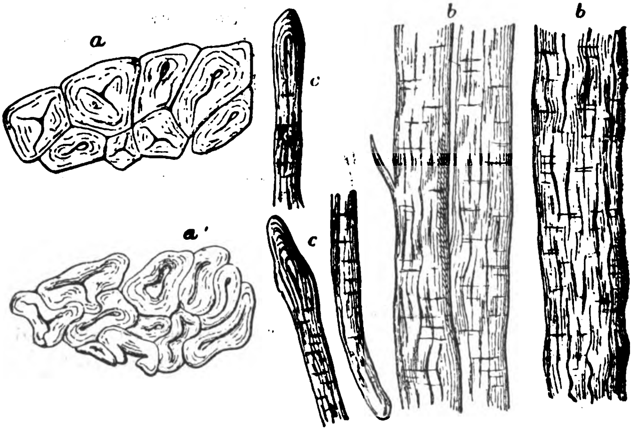

FIG. 7.

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[*] Chem. Soc. Journ. 1890, 57, 196.

Microscopic features.—Compact bundles. Fibres show striæ and fissures, and often fibrillæ, detached or adherent. The central canal almost obliterated; ends of fibres large and flattened. The bundles show fine transverse markings.

Section.—Well marked concentric zones of fibre-substance, irregular in outline.

Micro-chemical reaction.—Blue and yellow reaction with iodine solution, the joint result showing green coloration.

General chemical characteristic.—Pecto-cellulose.

Composition of Raw Fibre (Italian Hemp).

	Müller.
Cellulose	77·13
Fat and wax	0·55
Aqueous extract	3·45
Pectous substances	9·25
Water	8·80
Ash	0·82

Forms in which employed.—Scutching refuse, spinning waste, threads, cuttings and rope ends.

Sunda or Sunn Hemp.—Genus *Crotalaria*. Order *Papilionaceæ*. Bast filaments: length, 7–8 mm.; diameter, 0·03; ratio, 200 : 1.

Microscopic features.—Generally similar to those of hemp.

Micro-chemical reactions.—With iodine various, from blue to yellow. With aniline sulphate, slight yellow.

General chemical characteristics.—Pecto-cellulose (with some lignocellulose.

The following are the results of analysis of the raw fibre (H. Müller):—

Cellulose	80·01
Fat and wax	0·55
Aqueous extract	2·82
Pectous substances	6·41
Water	9·60
Ash	0·61

This fibre, exported from India and the Sunda Islands, has found employment in Spain and Portugal, but up to the present has not been adopted to any extent in other parts of Europe.

China Grass, Rhea, Ramie.—Genus *Böhmeria.* Order *Urticaceæ.* Bast filaments: length, 120 mm.; diameter, 0·05; ratio, 2400 : 1. Illustrated in Fig. 8: *a*, section of a bundle of fibres; *b*, a fibre seen longitudinally; *c*, ends; mag. 300.

Microscopic characteristics.—Irregular in form and length; often conspicuous in respect of latter (see Table, p. 88); fibre sometimes cylindrical, either smooth or striated, sometimes flattened; central canal well developed, often containing granules; extremities of fibres rounded, spatulated or lance-shaped. Sections marked by numerous concentric layers, often showing radiating striæ.

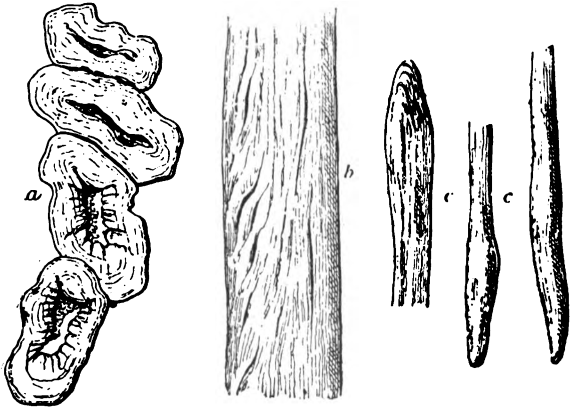

FIG. 8.

Micro-chemical reaction.—Blue to violet, with iodine solution.

General chemical characteristics— Pecto-cellulose.

Composition of raw fibre (H. Müller):—

Cellulose	75·83	62·50
Fat and wax	0·20	0·56
Aqueous extract	6·29	9·76
Pectous substances	6·07	12·00
Water	8·74	9·55
Ash	2·87	5·63

Forms in which employed.—This material has been the subject of successful experiments, which have resulted in a limited use of the fabric for papers of special character; imparts great tensile strength to paper. The portions available are as in flax.

Common Nettle.—*Urtica dioica.* Order *Urticaceæ.* Bast filaments: length, 27 mm.; diameter, 0·05; ratio, 550.

Microscopic characteristics.—Similar to the above.

The fibres of this plant were, in the olden times, separated in the same way as flax, and worked up into cloth. At present it has no practical interest to the paper-maker, but deserves attention at the hand of the student, as the most easily accessible for the purpose of study. It is, moreover, possible that, under cultivation, it may yet become a source of raw material for paper-making.

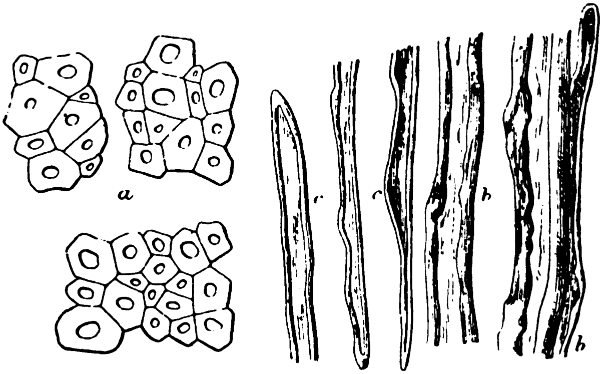

FIG. 9.

Jute.—*Corchorus.* Order *Tiliaceæ.* Bast: length, 2 mm.; diameter, 0·022; ratio, 90. Illustrated in Fig. 9: *a*, section of bundles of fibres; *b*, fibres seen longitudinally; *c*, ends; mag. 300.

Microscopic features.—Compact bundles; fibres smooth.

Micro-chemical reactions.—Yellow-brown, with iodine;

yellow, with aniline sulphate; bright yellow, with chlorine water; changed to carmine by treatment with sodium sulphite solution.

General chemical characteristic.—Lignocellulose. The chemistry of jute as the type of lignocellulose has been treated on pp. 53–60.

Composition of raw fibre (Müller):—

	1st Quality.	Cuttings or Butts. (Root ends.)
Cellulose	63·76	60·89
Fat and wax	0·38	0·44
Aqueous extract	1·00	3·89
Non-cellulose, or lignone	24·32	20·98
Water	9·86	12·40
Ash	0·68	1·40

Forms in which employed.—Threads, butts, bagging.

Bast Tissues.—We have alluded, in our opening remarks, to the broad division of the bast of exogens or dicotyledonous plants into coherent and non-coherent tissues. We have now considered the more important of the latter, and we find that they are obtained from the stems of annuals. We find also that while they constitute a tissue, in the sense of being definitely localised, the constituent fibres are disposed in parallel series of independent bundles or filaments, which are isolated by a mechanical operation after the whole stem has undergone the preparatory retting process. In exogens of longer and larger growth, the bast, as might be expected, becomes a coherent compound tissue, which is, in many cases, easily detached from the underlying wood. We shall mention three of these as receiving very important applications; though only one has been applied to any extent by the paper-makers of this country. This, which we shall consider first, is the bast of the *Adansonia digitata*, or baobab, a tree which flourishes in the tropical regions of the west coast of Africa. It is exported chiefly from Loanga, in the form of fibrous lumps of a brown colour. These are seen to be composed of a network of bast bundles, which are but slightly coloured, intersected by medullary rays of a dark brown colour. The microscopic features of the fibre are those which are generally characteristic of the bast of exogens; we do not know that we could cite any whereby it could be identified with certainty.

The fibres give a yellow coloration with aniline sulphate, but they contain only a small proportion of lignose. The following are the results of analyses of this bast:—

Cellulose	49·35	58·82 *
Fat and wax	0·94	0·41
Aqueous extract	13·57	7·08
Pectous substances	19·05	15·19
Water	10·90	13·18
Ash	6·19	4·72

LINDEN BAST (*Tilia Euorpæa*) is the raw material employed in the manufacture in Russia of the mats so largely used in this country for wrapping furniture and heavy goods, and also by gardeners for a variety of purposes. One of the features of this bast is the strong cohesion of the fibres in the bundles or filaments. They are resolved, but with difficulty, on long boiling, with a solution of carbonate of soda, the soluble products being of a mucilaginous nature. This bast has not been applied to any extent by the paper-makers of this country.

BAST OF THE PAPER MULBERRY (*Broussonetia papyrifera*).—This product deserves mention, not from its importance to the European paper-maker, but because of its application to the manufacture of the peculiar papers of the Chinese and Japanese. The special features of this, and the other basts which are similarly enployed in these countries—*Edgworthia papyrifera*, *Broussonetia kaempferia*, are (1) the ease with which the coherent fibrous tissue is separated from the parenchymatous tissue which accompanies it; (2) its comparative freedom from medullary rays; (3) the great length and fineness of the fibres. These properties conduce to its ready conversion into a well felted paper, of great tensile strength and remarkable softness.

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* Made up of { 13·75 cellulose from medullary tissue.
45·07 cellulose of fibres.

Class C.

The more important raw materials in this class are whole stems of monocotyledonous annuals. The isolation of fibres for paper-making from these plants depends upon a chemical process of resolution; the pulp obtained is, therefore, a complex of the various orders of cell-fibres contained in the plant. While the pulp consists for the most part of the vessels of the fibro-vascular bundles, it contains in addition the serrated cuticular cells which are so characteristic of this group. They therefore present a general similarity in microscopic features; there are, however, certain individual

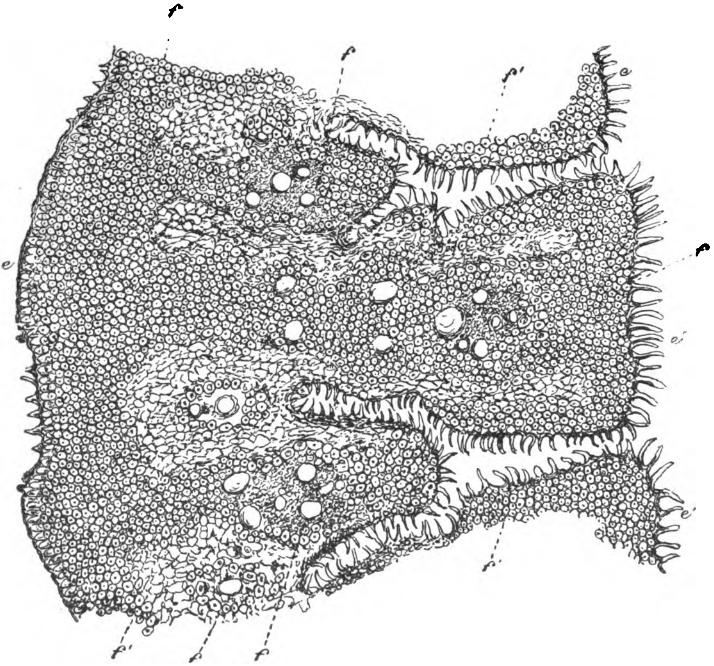

Fig. 10.

characteristics, such as the form and dimensions of particular cells, which serve for the identification of the various pulps. Where such occur they will be indicated.

Esparto.—*Stipa tenacissima* and *Lygeum Spartum.*

Order, *Gramineæ.* Bast fibres of fibro-vascular bundles. Length, 1·5 mm.; diameter, 0·012 mm.; ratio, 125. Illustrated in Figs. 10, 11. In Fig. 10, the fibro-vascular bundles *f* are seen spread throughout the interior of the leaf, but the intervals, instead of being occupied by parenchyma, with large cells and thin walls, are filled with a compact mass of fine solid fibres *f′*; *e*, external epidermis; *e′*, internal epidermis; mag. 100. In Fig. 11, *a* is a section of a group of fibres; *b*, fibres seen longitudinally; *c*, ends; mag. 300.

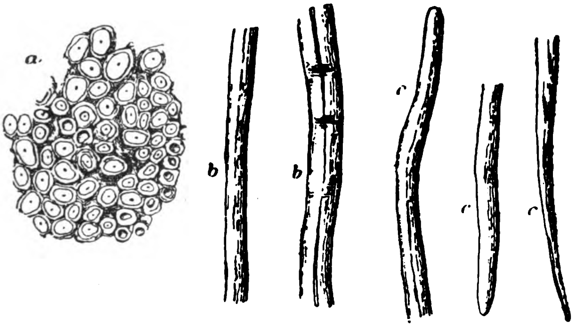

FIG. 11.

Microscopic features.—Short, smooth, cylindrical, uniform in diameter, central canal very small, extremities rounded, truncated and bifurcated.

Section.—Minute, generally oval, sometimes polygonal; central cavity represented by a point.

Micro-chemical reaction.—Both blue and yellow with iodine solution.

In examining a paper containing esparto under the microscope, the pulp will be found to contain, in addition to the fibres of the fibro-vascular bundles, a certain number of the cuticular cells (see Fig. 12), together with some of the fine hairs which are seen in the section (Fig. 10). These are very characteristic.

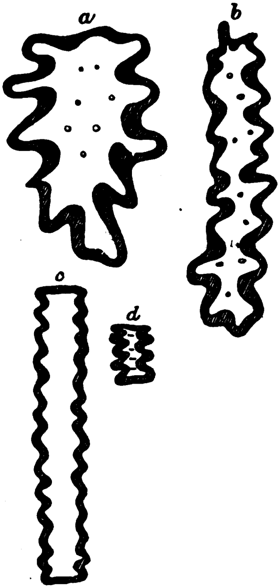

Fig. 12.

General chemical characteristics.—Pecto-cellulose mixed with some lignocellulose.

Composition (Hugo Müller):—

	Spanish.	African.
Cellulose	48·25	45·80
Fat and wax	2·07	2·62
Aqueous extract	10·19	9·81
Pectous substances, etc.	26·39	29·30
Water	9·38	8·80
Ash	3·72	3·67

Straw.—Order, *Gramineæ.*

Microscopic features.—Generally similar to those of esparto. There are, however, differences of shape and dimensions of the serrated cuticular cells, which differentiate the various kinds of straw from each other and from esparto.

In Fig. 12 are shown these cells, from maize-straw (*a* and *b*), from rye-straw (*c*), and from esparto (*d*). The following table gives the dimensions of the cells from different kinds of straw:—

	Length.	Breadth.
Barley . .	0·103–0·224 mm.	0·012–0·014 mm.
Rye . . .	0·086–0·345 „	0·012–0·016 „
Wheat . .	0·152–0·449 „	0·018–0·024 „
Oats . . .	0·186–0·448 „	0·012–0·017 „

Another distinctive feature of straw-fibre is the presence in it of a number of oval cells, derived from the 'pithy' matter attached to the inside of the stem. These are clearly shown at *b* (Fig. 13), which represents the general appearance of straw pulp.

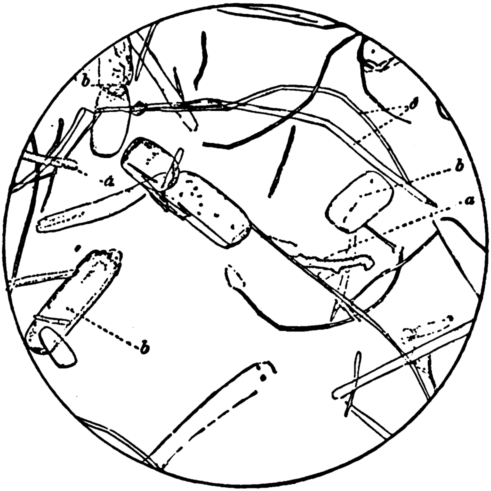

FIG. 13.

General chemical characteristics.—Both lignocellulose and pecto-cellulose.

The following are the results of analyses of straws (Hugo Müller):—

	Winter Wheat.	Winter Rye.
Cellulose	46·60	47·69
Fat and wax	1·49	1·93
Aqueous extract	8·07	0·05
Non-cellulose or lignin	28·49	26·75
Water	9·85	11·38
Ash	5·50	3·20

Bamboo and Sugar Cane.—Order, *Gramineæ.*

From the close botanical relationship of these products to the stems of the Gramineæ of our own climate, their microscopic features are, as might be expected, similar to those of straw. The similarity is further shown by the chemical composition (Hugo Müller):—

	Air-dried.
Cellulose	50·13
Fat and wax	0·78
Aqueous extract	10·56
Lignin and pectous substances	24·84
Water	8·56
Ash	5·13

New Zealand Flax.—*Phormium tenax.* Order, *Lineaceæ.* Fibro-vascular bundles of the leaves.

Microscopic characteristics.—Length of fibres, 9 mm.; diameter 0·016 mm.; ratio, 560. Fibres are fine, regular and smooth; the walls are uniform, central canal small, extremities vesicular. The fibres have little cohesion in the bundle. Sections round or polygonal.

Micro-chemical reaction.—Yellow, with iodine solution. Characteristic deep red coloration with concentrated nitric acid (Müller).

General chemical characteristic.—Lignocellulose. It contains 86·3 per cent. of cellulose.

Manila Hemp.—*Musa textilis*, Abacá. Order, *Musaceæ.* Fibro-vascular bundles of leaves.

Microscopic characteristics.—Length of fibres, 6 mm.; diameter, ·024 mm.; ratio, 250. Fibres, white, lustrous; the walls are uniform; central cavity large and very apparent. Fibres easily detached.

Sections round or polygonal. Illustrated in Fig. 14: *a*, section of bundle of fibres; *b*, fibres seen longitudinally; *c*, ends; mag. 300.

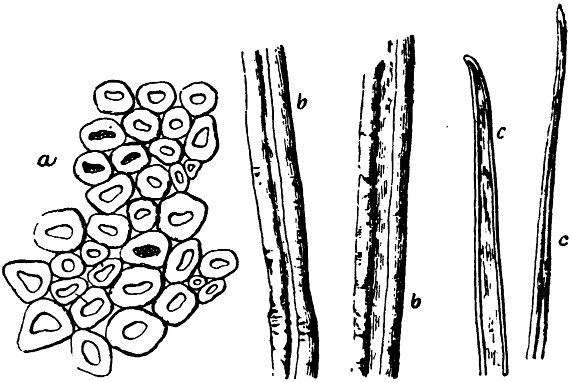

FIG. 14.

Micro-chemical reaction.—Yellow with iodine solution. Composition (Hugo Müller):—

Cellulose	64·07
Fat and wax	0·62
Aqueous extract	0·96
Lignin and pectous substances	21·60
Water	11·73
Ash	1·02

Wood.—Nearly, if not the whole of the chemical wood pulp used in this country is obtained from trees belonging to the order *Coniferæ* (Gymnospermæ), more particularly from the genera *Abies* and *Pinus*.

In America, however, poplar and other woods are largely employed. The coniferæ yield a larger proportion of pulp than most other woods, the individual fibres, moreover, are longer, and for these reasons it is generally preferred. On the other hand, however, poplar is more readily acted upon by reagents. Fig. 15 gives the microscopic appearance of the fibre of the common white fir. It is characterised by the presence of numerous pitted vessels (Fig. 15*a*).

Pine wood consists essentially of a compound cellulose, resembling in most of its properties the jute fibre (see p. 101).

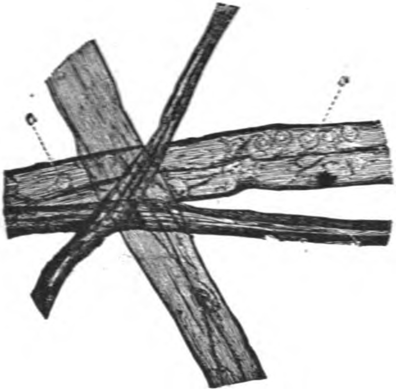

FIG. 15.

With iodine solution it gives a deep yellow colour. The chemical composition of some of the more important woods will be seen from the following analyses (Müller):—

—	Birch.	Beech.	Lime.	Pine.	Poplar.
Cellulose*	55·52	45·47	53·09	56·99	62·77
Resin	1·14	0·41	3·93	0·97	1·37
Aqueous extract	2·65	2·41	3·56	1·26	2·88
Water	12·48	12·57	10·10	13·87	12·10
Lignin	28·21	39·14	29·32	26·91	20·88

The above results are calculated on the ash-free wood. The ash varies from about 0·3 to 0·7 p.ct.

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* For the amounts of cellulose actually obtained in practice see 'Chemistry of Paper Making,' Griffin and Little.

CHAPTER V.

SPECIAL TREATMENT OF VARIOUS FIBRES; BOILERS, BOILING PROCESSES, ETC.

We have already discussed the principles upon which are based the chemical treatments of the various fibres for the isolation of cellulose, or of a partially purified fibre suitable for paper-making; of the two groups of processes, alkaline and acid, the former largely preponderate, fulfilling as they do a much wider range of conditions and attacking all the compound celluloses. The acid processes are for practical purposes limited at present to the treatment of woods by the bisulphites of lime and magnesia. The alkaline processes have the considerable economic advantage of allowing, by simple means, the recovery of the alkali. The waste liquors from the processes, when soda is used, are evaporated to a point at which the residual water does not prevent combustion of the organic matter, the burning off of which takes place in furnaces of various construction. The soda is thus recovered as carbonate ('recovered ash') or sulphide, and is available for further use.

The practice of these methods of recovery is obviously limited by the degree of dilution of the soda, whether in the liquors as obtained directly from the boiler, or in the wash waters from the 'boiled' pulp.

We now proceed to consider each fibre in detail, giving at the same time such information as is necessary regarding the preliminary treatment of the various fibres, and describing the forms of apparatus in which these operations are conducted. We shall consider the fibres in the order of their simplicity of treatment.

Rags (Linen and Cotton).—The treatment necessary for rags differs largely with the quality and, of course, with the kind of paper for which they are intended. These different qualities are known in the trade by different names and marks, such, for example, as the following:—New linen pieces, new cotton pieces, superfines, dark fines, grey linen, sailcloth, seconds, thirds, etc.

The two former consist of the cuttings produced in the manufacture of various garments, etc.; not having been worn, they are usually free from dirt, and are, in fact, if bleached, nearly pure cellulose, containing only the starch and other sizing material which has been added in the process of finishing the goods. They may, of course, contain considerable quantities of china clay or other loading material. In purchasing rags, therefore, regard should be had to the probable presence of these bodies. Such rags require only a very slight treatment; in fact, for certain classes of paper they might be used without any preparation. If, as is sometimes the case, the rags are unbleached, a rather more severe boiling is necessary.

It may be noted here that the removal of starch from 'rags,' i.e. cuttings of unused cloth, whether bleached or unbleached, is by no means easily accomplished by the ordinary alkali boil. The first effect of the treatment being to gelatinise the starch, which then combines with the alkali, the penetration of the rags by the alkaline lye is much impeded. The starch is best attacked by the specific treatment of malting. The rags are boiled with sufficient water to swell the starch; more water is then added to cool the mass to 60° C., and an infusion of malt is then added. In 1–2 hours the hydrolysis in the starch is so far complete that the ordinary boiling may be proceeded with after adding the complement of alkaline lye.

The greater part of the rags used in paper-making, however, consist of the residual portions of garments, household linen, etc., which vary in quality from clean, almost unused portions, to the very foulest sorts; the latter require a very drastic treatment. The first thing to be done with the rags is to 'sort' and cut them into convenient pieces. This is usually done by women, who stand at tables furnished with broad knives firmly fixed into them, with the backs towards the worker, and inclined at a slight angle. Near to the women are placed a number of boxes, corresponding with the number of qualities of rags, lined at the bottom with coarse wire gauze, into which the different sorts are put. The distinctions made are more or less arbitrary, but as a general rule the rags are sorted with special reference to their colour and the material of which they are composed, which in turn are essential factors of the degree of chemical treatment required. The coloured rags may be allowed to accumulate, and then made into a coloured paper. During the process of cutting, all hard substances, such as buttons, pieces of iron, etc., are carefully removed. The rags are cut into pieces of

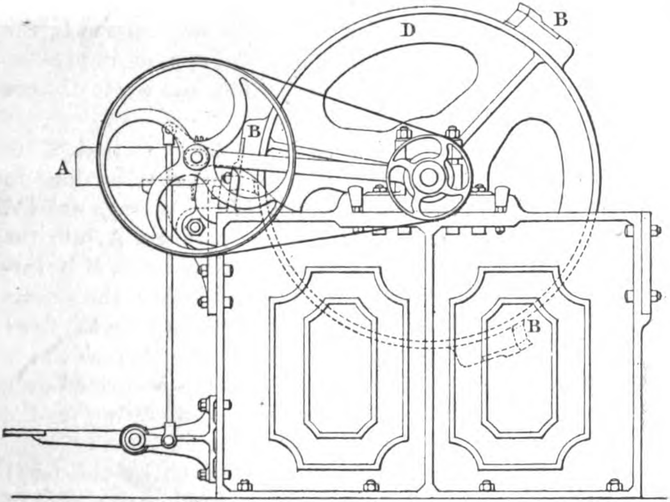

FIG. 16.

from two to five inches square. In some mills machines are used for cutting.

Fig. 16 shows the construction of a machine that may be used either for rags or rope. The material is passed into the machine along the table A, where it passes between the stationary knife C and the knives B, fixed in the revolving drum D. The cut rags fall into a receptacle placed underneath the drum.

Notwithstanding the extra expense of cutting by hand, it is nevertheless preferred by many, especially for the finer grades of paper. One reason for this is to be found in the fact that more perfect sorting and removal of impurities can be effected. It is moreover said that less waste of fibre occurs in the subsequent operations.

The next process which the rags undergo is that of removing all loose extraneous matter. This may be done in a machine such as is shown in Fig. 17. The rags are fed continuously by the endless travelling platform A into the willow. This consists of two wrought-iron drums, B B, furnished with wrought-iron teeth C, which, when the drums revolve, pass rapidly near to the stationary teeth fixed into the cast-iron framework of the willow. The sides are covered in with cast-iron doors, and the top is covered over with sheet iron. Underneath the drums is a grating for the escape of dust.

The rags, having been thoroughly beaten by the teeth of the drums, pass into the duster D, consisting of a kind of hollow cylinder E, made of strong iron bars securely fastened to the circular ends F, the bars being covered with wire cloth or perforated zinc. It is made to revolve almost horizontally, a slight dip being given to it in order that the rags may be carried forward to the lower end. The bars or skeleton of the cylinder are furnished with a number of teeth securely bolted on. The whole is enclosed in a strong wooden box in which it revolves, and which serves to collect the dust passing through the wire cloth. The cylinder E is driven by the gearing G. This combined willow and duster may be used for dusting and cleaning not only rags, but almost any other kind of fibre. The willow and duster sometimes form two separate machines.

The cleaned and dusted rags are now ready to be boiled, although it is the practice in some mills to give them a preliminary washing with water.

The boiling may be conducted either in spherical or cylindrical boilers, or in the ordinary vomiting boilers described under Esparto. (See p. 125.)

In Fig. 18 is shown, part in section and part in elevation, a spherical rag-boiler, as manufactured by Messrs. G. and W. Bertram. This boiler, of from 8 to 9 feet diameter, is supported by means of the hollow journals A on the standards B and is made to revolve by means of the gearing C.

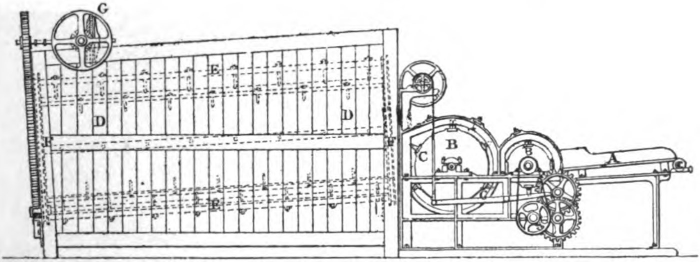

FIG. 17.

Steam enters by the pipe D, which is fitted with a safety-valve E, and vacuum valve F. The steam on entering the boiler is distributed by means of the 'baffle-plate' G. Lye enters by the pipe H. The boiler is fitted with two doors I, wherewith to fill and empty; the waste lye is run off by the cock J. L is a small blow-through cock. The false bottom K prevents the rags from choking up the cock, and also serves to drain off the waste liquor.

The alkali employed may be either caustic lime, caustic soda, sodium carbonate, or a mixture of the latter and lime, which is of course equivalent to using caustic soda. The proportion of alkali depends upon so many considerations that it is quite impossible to give exact information on this point. In the case of caustic soda, a quantity equal to from 5–10 p.ct. on the rags may be taken to be a fair average. If lime be used it should be slaked with water, made into a thin milk, and carefully filtered through fine wire cloth. to keep back the particles of sand, coal, etc., which lime is always liable to contain. From 5–10 p.ct. may be used. The amount of lime actually dissolved in the water is relatively small (1·3 grm. per litre); the portion in solution, however, rapidly combines with the grease, dirt and colouring matter of the rags and forms with them insoluble compounds, a fresh portion of lime being at the same time dissolved. This formation of insoluble compounds constitutes an important objection to the use of lime, as they are liable to remain to some extent fixed in the rags and are with great difficulty removed by washing. For this reason, therefore,

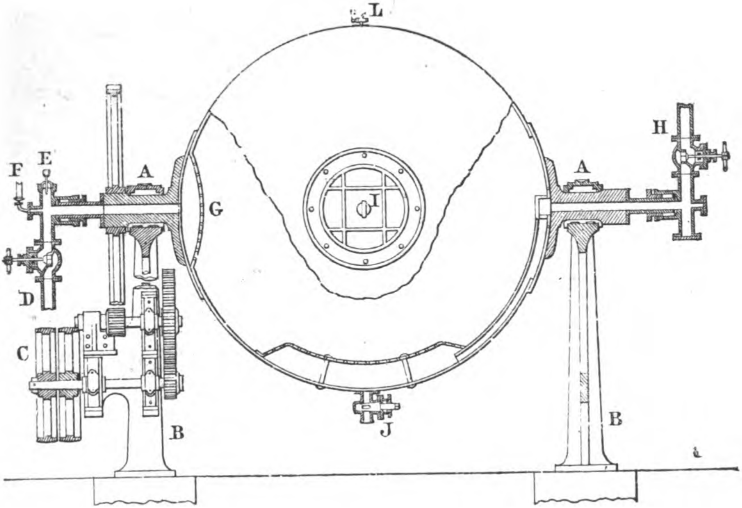

FIG. 18.

the more soluble alkali is to be preferred. Moreover, the lime sometimes tends to exert a hardening effect upon the cellulose. Notwithstanding these objections, lime is used by some paper-makers in preference to soda. In making choice of the chemical for boiling, much depends on the quality of the rags and the nature of the paper for which they are intended, so that no fixed rules can be given.

To reduce the treatment of rags to 'first principles, the paper-maker requires to inform himself of the chemical treatments adopted in the textile industries, whether in *bleaching* the goods or in dyeing and printing them. As regards the former, he requires to follow the same line of treatment; and in the removal of colour from dyed and printed goods, a knowledge of the method by which the colour was fixed will enable him the more economically to undo that process.

The time of boiling varies from 2 to 6 hours, according to the quality of rags, the chemical employed, and the pressure. The use of very high pressures should be avoided as far as possible, as there is a danger, owing to the correspondingly high temperature, of *fixing* the dirt and colouring matters instead of dissolving them.

The quantity of water should be kept as low as may be, in order to have as strong a solution of alkali as possible; this effects a saving both in the time of boiling and in the alkali, and this is of great importance where it is necessary to evaporate the whole of the waste liquors. It should also be remembered that a certain amount of water is always formed by condensation in all boilers in which live steam is used. On the other hand, if too little water be added, the rags are liable to become 'burned' and the fibre therefore weakened. During the operation the boiler should be made to revolve slowly, in order to produce thorough circulation of the liquor.

The boiling being completed, the pressure is allowed to fall, either by cooling or by blowing off from a cock usually provided for that purpose, and the liquor allowed to collect at the bottom of the boiler. It is then run off by the cock J (Fig. 18), and the rags drained as much as possible. Water is then run in to give the rags a preliminary washing. If time permits the steam may be turned in and the operation assisted. After again draining, the rags are withdrawn from the boiler into any suitable receptacle. A convenient form is that of a rectangular iron box on wheels, which can be readily transferred from one part of the mill to another.

The next process is that of washing. This is usually performed in a washer or breaker, the construction of which is shown in Fig. 19.

It consists essentially of a rectangular vessel with rounded ends, in the centre of which, but not extending the whole way, is a partition B, known as the 'mid-feather.' The roll A, which is furnished with a number of steel knives G, and driven from the wheel H, revolves in one of the compartments formed by the mid-feather. In this compartment the floor is inclined in such a way as to bring the pulp well under the roll, as shown by the dotted line D. Immediately under the roll is what is called the 'bed-plate,' the end of which is seen at I, extending up to the mid-feather, and fitted with knives similar to those in the roll A. The arrangement of the knives, both in the bed-plate and the roll, is similar to that given in Figs. 33 and 34. The distance between the roll and the bed-plate can be varied at will by means of the handle E, which is so arranged as to raise both ends of the roll simultaneously. In those breakers of an older pattern, one end only of the roll was raised, and thus the knives became worn unequally.

After passing between the roll and the bed-plate, the pulp flows down the 'back-fall' D', and finds its way round to the other side of the mid-feather. On the inclined part of the floor, and immediately in front of the bed-plate I, a small depression is made, covered with an iron grating, for the purpose of catching buttons, small pieces of stone, and other heavy substances that may have found their way into the rags. There is generally a similar grating with rather finer openings on the other side of the mid-feather. The engine is constructed of iron, generally made in one casting.

The dirty water from the rags is removed by the 'drum-washer' C. It is divided into compartments by the partitions shown by the dotted line *c*. The centre of the drum is formed of a conical tube, the narrow end of which is towards

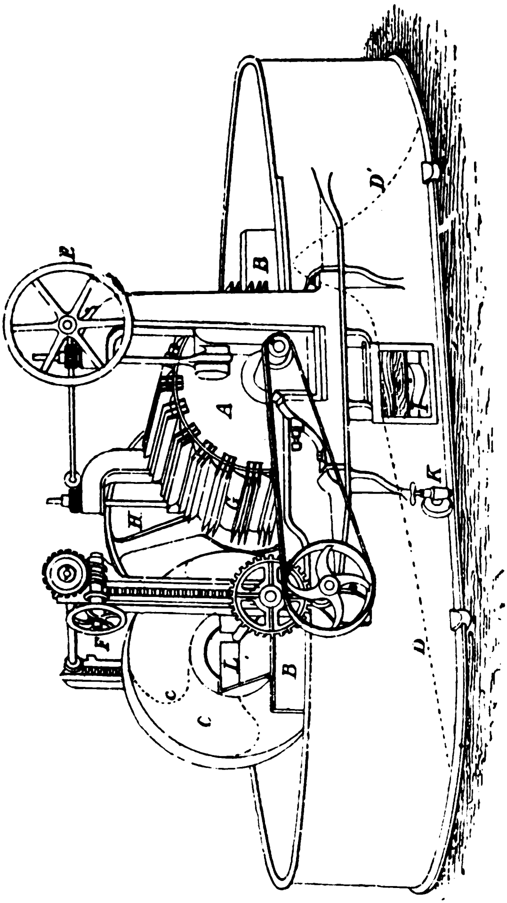

FIG. 19.

the mid-feather. The ends of the drum are generally made of mahogany, as this is found to stand the action of alkali better than any other wood. The periphery is covered with fine copper or brass wire-cloth, laid on to a backing of a much coarser material. An improved form of backing has been introduced lately, which is much more durable than wire. It is formed of brass cut into the form shown in Fig. 20. The drum can be raised or lowered by the small wheel F, and it is driven by a belt on the shaft that bears the roll.

The wash-water passes through the wire cloth into the compartments formed by the partitions *c*, and finding its way down to the narrow end of the inner conical tube, flows out through the side of the drum into a trough which is placed across the washer to receive it. Or it may, as shown in the drawing, be conducted through the mid-feather itself, which is made hollow at this part for the purpose.

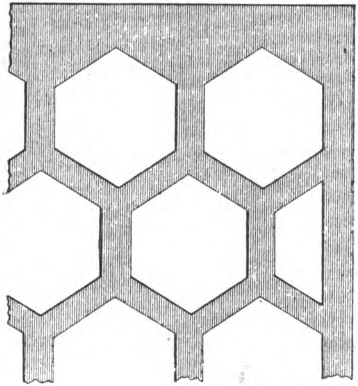

FIG. 20.

Another form of drum-washer, called the siphon-washer, is sometimes used. Its construction will be understood by reference to Figs. 21 and 22.

The drum is simply a hollow cylinder of wire cloth, the ends of which are formed of wood. Inside the cylinder is the siphon tube A, into which the water passing through the wire cloth flows. The continuation of the siphon tube B (Fig. 22) is made of flexible tubing. The action of the siphon is commenced by filling it with water through the cock C (Fig. 22). The water then flows in the direction indicated by the arrows. The tube A is fixed, and passes through a hollow journal fitted on to the end of the drum. The other end is connected with the rod E, on which the driving pulley D is placed.

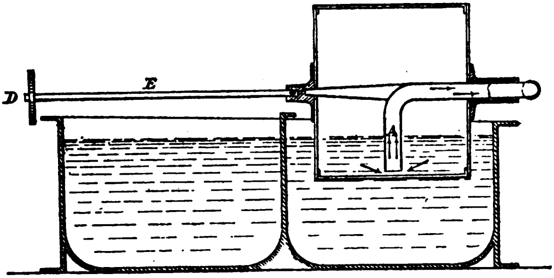

FIG. 21.

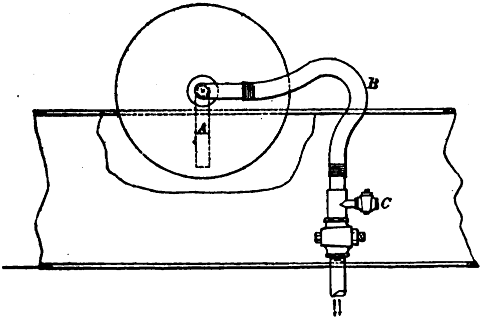

FIG. 22.

The water passing through the wire cloth on the drum carries with it a certain amount of fibre which, unless special precautions are taken (see 'Save-all,' p. 221) is lost. The amount is considerable in the case of weak rags, and care should therefore be taken that the washing is not prolonged more than is consistent with proper cleansing, and that the pulp should not be too much broken up at this stage.

The washed and broken pulp goes by the name of 'half-stuff.'

The following is the usual plan of treating rags in the washer: it is first half filled with water, and the rags from the boiler put in gradually until nearly filled. Water is now allowed to flow in at the opposite end to where the drum-washer is placed. This, by the action of the roll, mixes thoroughly with the pulp and extracts all the soluble matter, and also carries with it fine insoluble impurities.

The action of the knives in the roll on the rags passing between it and the knives in the bed-plate serves to break them up and thoroughly disintegrate them. The dirty water then passes away through the drum-washer, the stream of pure water being regulated so as to keep the level constant. This is continued until only pure water passes away. The supply is then stopped, the washer still being kept in action. As the level falls the drum is lowered by means of the handle F. When sufficiently drained the pulp is discharged through a valve in the bottom of the engine. It is now ready to be bleached. This may be done in separate engines called 'potchers,' somewhat resembling the breaker or washer already described, or it may be done in the breaker itself. The process of bleaching will be described in Chapter VII.

Occasionally the bleaching process is conducted in the 'beater' itself, but this is not to be recommended.

Esparto.—This raw material, on account of its high percentage of non-cellulose constituents, requires a large amount of soda to resolve it; on the other hand, being of the nature of a pecto-cellulose, the process of disintegration may be conducted at a low pressure; in fact, it is the practice at some mills to boil in open vessels, in which case, however, a larger amount of soda is required. As has been already stated, it may be taken as a general rule for all fibres, that within certain limits the higher the pressure employed the less soda is required. The quantity necessary again varies with the various qualities of esparto, which depend in the first instance upon the country or district of origin of the grass. Caustic soda is the chemical invariably employed; lime, on account of its forming insoluble compounds with the non-cellulose portion of the grass, is inapplicable. Not only does the amount of soda depend upon the pressure, but it also depends to a considerable extent on the form of boiler employed. The use of rotary boilers is objectionable, as the esparto tends to collect together into compact masses, which are with difficulty penetrated by the liquor. It is therefore the almost universal practice to employ stationary boilers, in which an automatic circulation of the alkaline lye is maintained on what is technically known as the 'vomiting' principle.

The first treatment that the esparto undergoes is that of 'picking.' The bands of the bales in which esparto is packed, generally by hydraulic pressure, are cut, and the grass is spread out on tables by women, who carefully remove such impurities as weeds, root-ends, etc., which from their nature are with great difficulty boiled and bleached, and which if not removed would be liable to appear in the finished paper as dark-coloured specks, technically known as 'sheave.' This treatment is called 'dry-picking,' in contradistinction to a subsequent process, known as 'wet-picking.' A portion of the table is covered with coarse wire gauze, through which, when the grass is spread over it, loose particles of sand, dirt, etc., escape. The cleaning of esparto can be much better accomplished by means of machinery. Fig. 23 is an elevation of a machine manufactured for the purpose by Messrs. Masson, Scott & Bertram. The grass, which may be in the form of sheaves, as taken from the bales, is put in by the hopper A. It passes thence to a conical drum made of steel bars placed very close together, driven rapidly by the shaft B. It is provided with five rows of teeth. Fixed to the sides of the willow there is also a row of stationary teeth. The grass is thoroughly broken up and dusted by the action of the teeth, and is transferred to the wide end of the willow at C, where it is carried forward on the travelling tables D. During its passage along the tables it can be examined and picked by women standing on the platforms E. The dust and dirt passing through the steel bars of the drum are drawn away by a fan through the pipe F.

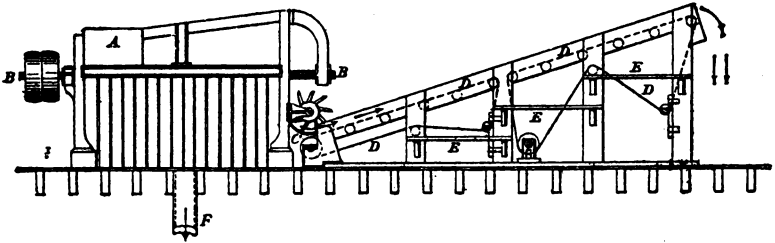

FIG. 23.

This machine is also adapted so as to carry the cleaned grass to the boiler-house. It is taken forward by means of travelling rakes over the tops of a series of boilers, any one of which can be furnished by simply opening a door corresponding in position with the lid of the boiler.

Boiling.—The ordinary form of boiler is shown in Fig. 24. It is known as a vomiting boiler. The grass is put in by the door E, which is hinged and is counterbalanced by the weights L. It is securely fastened down by the screws F. Steam enters by the inner pipe A, which dips a little below the perforated false bottom B. Surrounding the steam-pipe is a wider pipe C, open at the top, which is made slightly trumpet-shaped; also open at the bottom, where it ends in a kind of shoulder, on which the false bottom rests. The lower part has two or more openings G cut away, through which the liquid can freely pass.

In order to get as large a charge into the boiler as possible, steam is turned on while furnishing, and a quantity of caustic soda lye is also run in, which has the effect of softening the grass and making it more compact. This is continued until the boiler is well filled.

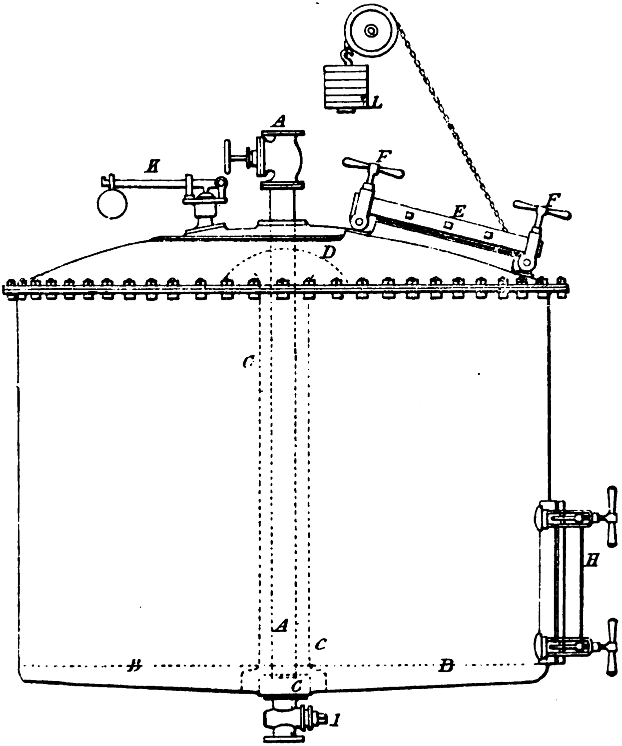

FIG. 24.

The action of the boiler is as follows:—The steam, passing through the pipe A, heats the liquor that has drained from the grass through the perforations in the false bottom, and, forcing it up the wide pipe C, causes it to strike against the dome or bonnet D, and distribute itself again over the grass. This constitutes the 'vomiting' process of circulation of liquor.

The boiler is emptied by the door H, and the liquor is run off by the cock I. The boilers are usually supplied with a safety valve E, and also with a pipe for letting off the steam when the boiling is finished. The boiling generally takes from 4 to 6 hours. The quantity of soda necessary depends upon the nature of the grass, Spanish requiring less than African.

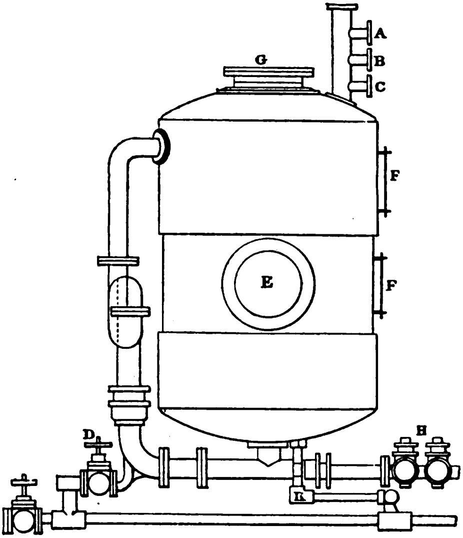

FIG. 25.

Routledge, to whom the introduction of esparto as a paper making material is due, gives 10 p.ct. as the proper quantity.

The pressures employed vary from 5 lbs. to 45 lbs. There has been a growing tendency of late to employ the higher pressures, for reasons already stated.

Of late years great improvements in the form of the boiler have been introduced. Fig. 25 is an illustration of Roeckner's Patent Boiler. The vomit pipe is outside the boiler. Steam entering by the cock D, forces the liquor up the vertical vomit pipe and distributes it over the grass. The pipe K is used for heating the liquor at the commencement of the operation by means of waste steam. F F are

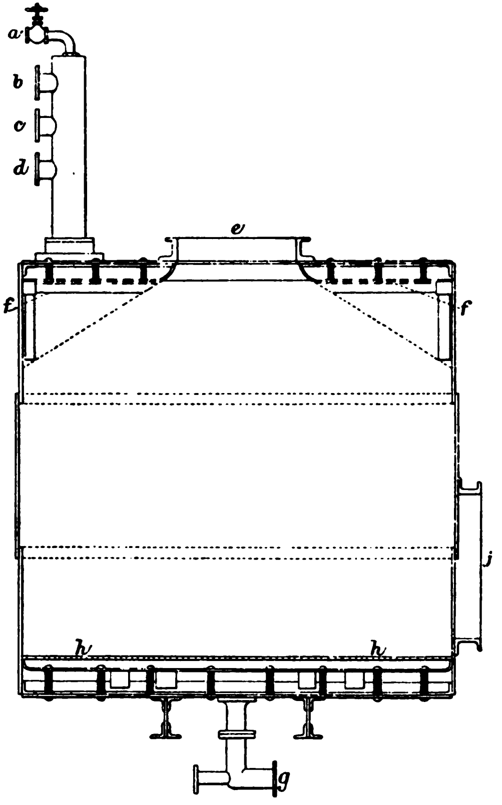

Fig. 26.

gauges for indicating the height of the liquor. The grass is put in by the opening G. The pipes A, B and C are for the supply of steam, strong lye and water. The boiled grass is discharged by the circular door E.

The boiler holds three tons of grass, and the boiling is completed in about 2½ hours, the pressure being about 35–40 lb. per square inch. It is claimed that by its use a saving both of time and soda is effected.

Sinclair's Patent Boiler is shown in Fig. 26. The vomit pipes, of which there are two, are made of thin steel plates riveted to opposite sides of the boiler. The liquor drains through the perforated false bottom, and is then forced up the vomit pipes above the perforated plates, through which it is distributed over the grass in a number of fine jets. The boiler is charged by the door *e* and emptied by *j*. The small cock *a* is used as a blow-through cock; the opening *b* is used for blowing-off steam when emptying the boiler; *c* for letting in caustic soda lye; *d* for water. Steam enters by the small branch of the T pipe at the bottom of the boiler, the other, *g* being used for running off the waste liquor. A boiler holds from two to three tons of grass, and a boiling is completed in about two hours at a pressure of 40–50 lb. per square inch. Under these circumstances it is easy to conduct four complete operations in one boiler in the twenty-four hours; the time required for filling and emptying being one hour each.

The two forms of boiler above described possess the obvious advantage of having the whole or nearly the whole of the interior available for holding grass; the boilers can therefore be made to hold more, and the boiling is moreover much more evenly accomplished.

Washing.—The boiling being completed, the steam is allowed to escape and the liquor to collect at the bottom of the boiler, where it is run away by the pipes placed at the bottom for the purpose. Water is then run in and steam turned on for a short time; this is also run off, and the grass drained as completely as possible. The boiled grass is then emptied into trucks and taken away to the washing engines. These resemble those already described under Rags.

During the process of washing, a certain amount of the shorter fibres find their way through the meshes of the wire-cloth. In addition to this, a large proportion of the cellular tissue surrounding the fibro-vascular bundles (see Fig. 10, p. 104) is carried away. If the wash-water be examined under the microscope, it will be seen to consist largely of this cellular matter. Though this entails a certain loss of cellulose, its removal is in other respects advantageous, as it is possessed of hardly any 'felting' properties, and it is moreover exceedingly difficult to bleach.

The amount of fibre actually obtained in practice is but little below that contained in the grass. A certain loss is inevitable, but this probably does not exceed 1 or 2 p.ct.

The percentage of cellulose in esparto is given on p. 106. The following numbers obtained by the authors are somewhat higher. They are calculated on the absolutely dry fibre; those mentioned are on the *air-dry* samples:—

	Cellulose per cent.
Spanish	58·0
Tripoli	46·3
Arzew	52·0
Oran	45·6

There is no doubt that considerable differences occur even between different specimens of the same kind of grass.

It is the practice in some mills to wash the grass in a series of tanks connected together in the same way as the lixiviating tanks of an alkali works. They are so arranged that pure water flows in at one end, passes through fresh lots of grass in succession, and issues at the further end highly charged with the soluble products of the grass. By such an arrangement the grass can be washed without any loss of fibre, and with a minimum quantity of water. This latter feature is of great importance in mills where it is necessary to evaporate the whole of the waste liquors from the esparto, as they are then obtained in a very concentrated form. Even with such an arrangement it is advisable to give the grass a short final treatment in the washing engine.

The washing having been completed, and the esparto having been broken up into 'half-stuff,' it is now ready to be bleached (see Chap. VII.).

The presse-pâte system, originally adopted for the treatment of straw, has of late years been extensively applied to esparto.

The presse-pâte consists of the wet end of a paper machine, and is furnished with sand-tables and strainers. The pulp is allowed to flow on to the wire cloth, so as to form a thick web of pulp. The bulk of the water passes away through the wire cloth; a further quantity is removed by the vacuum-boxes and couch-rolls. The pulp, containing from 50 to 60 p.ct. of water, is wound round an iron rod until a sufficiently large roll is formed.

The advantages of the presse-pâte system are the possibility of the removal of dirt and unboiled portions by means of the sand-tables and strainers, and the very complete washing and removal of the products of the action of bleaching powder.

It also enables manufacturers to dispense with the somewhat costly methods of dry and wet picking.

The presse-pâte system can also be applied to the unbleached pulp.

It may be interesting at this point to say something about the substances which are removed from the esparto by the caustic soda. On referring to p. 106 it will be seen that the original grass contains nearly half its weight of non-cellulose, the removal of which has to be effected. Only a small proportion of this is 'extractive matter' in the ordinary sense of the term, i.e. that can be extracted by the usual solvents; the remainder is intimately combined with the cellulose. The action of the caustic soda is to resolve these bodies, the cellulose remaining behind, and the other constituents being dissolved as 'resinous' bodies by the soda. A certain proportion of the mineral constituents, notably the silica, dissolves in the lye, the latter forming silicate of soda.

On neutralising the liquor with an acid, the bulk of the dissolved constituents is thrown down as a dark brown resinous mass. If this crude product be purified, it is found to consist of a definite body having the formula $C_{21}H_{42}O_2$. By the action of chlorine on this resin a bright yellow chlorine compound is formed, resembling the compound from jute described on p. 55. If the resin be treated with concentrated nitric acid, a bright yellow body is formed, which forms definite compounds with bases, and which has the property of dyeing animal fibres a bright orange colour. In addition to this body, a yellowish-white wax can be isolated. It sometimes happens that this wax is but imperfectly dissolved in the caustic lye; if the waste liquor be allowed to stand, the wax is occasionally found to collect in small quantities on the surface.

Various attempts have been made from time to time to remove from the waste liquors the soluble matter derived from the esparto by the addition of lime. This throws it down, in fact, as a very voluminous precipitate, exceedingly difficult of filtration. The filtrate contains only caustic soda. The difficulties of removal of the precipitate, however, are almost insurmountable. The usual method of disposing of the liquor is to evaporate it to dryness and ignite it, as will be subsequently described under the head of 'Soda Recovery,' Chapter XI.

Another by-product deserving specific mention is acetic acid, which is formed to some extent in the boiling process, but in much greater proportion in the further evaporation of the liquor, and charring the residue. The production of acetate is a maximum when the temperature of charring does not exceed 350°. The acetic acid is obtained as sodium acetate on lixiviating the char, the yield of the salt amounting to 5–6 p.ct. of the weight of the original esparto. Such a process was patented by W. H. Higgin in 1891,* and the

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* English Patent 13,409.

above results verified by operations on the large scale. But the process has not been practically adopted.*

Straw.—Straw very closely resembles esparto in its chemical constitution; it is, however, more highly lignified, and for this reason (see p. 57) requires a more drastic treatment for its resolution. It is therefore usual to treat straw with rather larger quantities of caustic, and generally at high pressures. It is possible, however, to resolve it at 5–10 lbs. pressure, but the resulting pulp is more difficult to bleach, and can only be used for inferior kinds of paper. In treating straw for use in high-class paper, i.e. for the isolation of a 'pure' straw cellulose, it is necessary to boil under such conditions that even the knots, which are much less readily attacked, shall be so far disintegrated that they may be bleached with a moderate quantity of bleaching powder. Such a treatment, on the other hand, involves a diminished yield of pulp, and at the same time a somewhat weakened fibre.

The kinds of straw in general use are wheat, oat, rye, and barley; the two first constituting the bulk of the raw material, at least in this country. Some idea of the composition of straw may be gathered from the analyses given on p. 108.

It will be seen that the amount of cellulose is quite as high as in esparto, but for the reasons above given and from the fact that a large proportion of the cellulose consists of cellular tissue (see Figs. 12 and 13), which is easily attacked by soda and readily passes through the meshes of the drum-washers and the wire-cloth of the presse-pâte and paper machine, the yield obtained in practice falls considerably below that from esparto.

In addition to the numbers already quoted on p. 108, the following results of analyses made from time to time by the authors, may be interesting. The percentages are calculated on the absolutely dry material.

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* See also 'On the Production of Acetic Acid from the Carbohydrates,' Journ. Soc. Chem. Ind. v. 11.

		Cellulose per cent
Oat straw		52·0
„		53·5
Wheat straw		49·6
Rye „	(foreign)	53·0
Oat „	„	46·5
Wheat „	„	50·2

The yield of pulp is greatly influenced by the conditions under which it is obtained; high pressures and temperatures exerting considerable influence on the result. This is probably the case with straw more than any other fibre, on account of the physical and chemical nature of the cellulose. It is doubtful whether much more than 35 p.ct. is actually obtained in practice.

Straw is usually boiled in cylindrical rotary boilers. Some paper-makers, however, prefer to use one or other of the different forms of vomiting boilers already described.

The use of a rotary boiler is open to certain objections. In the first place, it is doubtful if they are as economical of soda as the vomiting boilers, especially the more recent patterns; and, secondly, the rotation of the boiler so disintegrates the pulp, that a certain proportion of the cellulose, especially those fibres which are short, is liable to be lost during the subsequent treatment. It seems probable that the best results would be obtained if the rotation of the boiler were reduced to a minimum, in fact, sufficient only to produce thorough circulation of the liquor.

The proportion of soda necessary to boil straw thoroughly is, for reasons already stated, greater than is the case with esparto. The amount varies from 10 to 20 p.ct. on the raw material.

The different processes to which straw is subjected vary greatly. The following may be taken as a general indication of the methods employed. The straw is usually cut into short pieces of about 1–2 in. in length by means of an ordinary chaff-cutter. The cut straw is carried by means of a blast of air along a wooden tube or shaft into a chamber, the sides of which are made of coarse iron gauze. This chamber is itself enclosed in another chamber, in which the dust and dirt accompanying the straw collect. The clean straw is then placed in sacks and conveyed to the boiler-house.

Owing to the bulky nature of straw, it is difficult to get a large charge into a boiler at one operation; it is therefore usual, after having filled it as completely as possible, to run in a portion of the lye required, and to turn on the steam for a few minutes. This has the effect of so far softening the straw as to make it lie closely at the bottom of the boiler and to allow of a further quantity being put in. This having been accomplished, the remainder of the lye required is run in, together with the requisite quantity of water, and the steam turned on. The pressure may vary from 10 to 50, or even 80 lbs. per sq. in., and the time from 4–8 hours.

When the boiler has sufficiently cooled, the charge is run out by a cock in the bottom. Owing to the rotary action of the boiler the straw is in the state of fine pulp, having been almost completely disintegrated; so fine, in fact, that it flows readily through a 3-in. pipe. It is run into large tanks with perforated tile bottoms, where the excess of liquor is allowed to drain away and the pulp washed by the addition of water. It is then dug out and taken to be bleached. Before this is done, however, it may be necessary to give it a further washing. This may be done in the potcher itself. Instead of washing the straw in tanks, it may be washed in an ordinary washing engine, such as has been already described. Owing to the finely divided state of the pulp, however, this method, unless the meshes of the wire-cloth covering the drum washer are very fine, entails a considerable loss of fibre. It is more suitable in cases in which the straw has been boiled in stationary boilers, and in which therefore it is less disintegrated. When stationary boilers are employed, it is not necessary to cut the straw very fine; in fact, it is sometimes put into the boiler whole. The cutting has this advantage, that it loosens the adhering dirt. In cases where the action of the soda has not been carried far, or the straw has been put into the boiler whole, the pulp will not be disintegrated to the same extent, and will not flow through a narrow pipe. It is necessary therefore to discharge the boiler through the doors used for filling.

A novel form of washer especially adapted for straw, whereby the washing is effected with the minimum quantity of water, has been used on the Continent to a considerable extent, and in some mills in this country. The pulp is caused to pass along a series of revolving cones covered with wire-cloth, through which the liquor escapes. As it reaches the end of each cone, the pulp is emptied into a small tank containing water from the cones further on in the series. It is carried forward by means of hollow bent arms connected with the inside of the next cone, which then discharges it at the other end, to be again carried forward.

As already stated, the presse-pâte system is largely adopted for straw pulp; it has been described under Esparto. It may sometimes be employed with advantage before bleaching, though it is generally used after.

A method of treating straw is sometimes adopted which produces a pulp of higher quality than is obtainable by the ordinary method. The washed pulp is mixed in a chest provided with stirrers, with a large quantity of water, and is then pumped into another chest placed at a higher level, from which it flows between a pair of hard granite millstones, the surfaces of which are cut into radial grooves. The stones are fixed horizontally, and are made to revolve at a very rapid rate. During the passage of the pulp through the stones, the knots, weeds and other hard portions of the straw which may have resisted the action of the alkali are reduced to a fine state of division, and are thus more readily acted upon in the subsequent operation of bleaching. The degree of fineness to which the pulp is reduced can be determined by regulating its flow and the distance between the stones. Pulp produced in this way is of a very even character, and is comparatively free from unbleached particles.

Within recent times a process of treating straw has been introduced which, on account of the high quality of the pulp produced, has attracted considerable attention from paper-makers. It consists in exposing pulp obtained in the usual way by the action of caustic soda to the action of chlorine gas.* The amount of soda in the preliminary boiling is reduced much below that necessary for perfect pulping, the result being that the cellulose is much less liable to be destroyed, and thus a greater yield is obtained. The pulp is thoroughly washed and partially freed from moisture in a centrifugal machine until only about 70 p.ct. remains. The partially dried pulp is then exposed in leaden or stone chambers for some hours to an atmosphere of chlorine, produced by the action of hydrochloric acid upon manganese dioxide. By the action of the chlorine, those portions of the straw which have been but imperfectly acted upon by the caustic soda in the boiling process are completely disintegrated, or, rather, are rendered more susceptible to the action of the bleaching liquor employed subsequently. The consequence is that when bleaching liquor is added, the whole of the straw is rapidly reduced to the state of pure cellulose, and the finished product is remarkably free from anything like unbleached portions. Owing to the fact that the action of the caustic is minimised, a considerable portion of the more easily degraded cellulose survives, and the yield of the pulp is thereby increased. The process is, however, necessarily expensive. The action of the chlorine will be readily understood by a reference to p. 55.

Owing to the fact that a considerable proportion of the pulp obtained from straw consists of cellular tissue (see Fig. 13, p. 107), which, although cellulose, is devoid of fibrous structure, paper made from straw only is found to be much weaker than that made from fibres such as esparto. On the other hand, being a cheap material, and one capable of yielding a very white pulp with a moderate quantity of bleach, it is held in considerable repute by many paper-

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* English patent, 938, 1880.

makers, especially as a material for mixing with esparto. It is sometimes mixed with cotton and linen rags, even in the finest qualities of paper.

Straw cellulose is distinguished by its capacity for hydration and partial gelatinisation under the action of 'beating.' As a consequence, it adds the quality of 'wetness' to the pulp, which again confers the quality of hardness and 'rattle' upon the finished paper.

Wood [Wood cellulose, or 'chemical wood pulp'].—The treatments of the wood by the alkaline processes are comparatively simple operations. Owing to the powerful and general action of caustic soda the hard material requires no special treatment for removing such more resistant structures as knots, or again, rotten wood, both of which survive the bisulphite processes more or less unattacked. The bark is stripped and the wood chipped and passed through a mechanical 'duster' to the boiler or digester. These are of the ordinary types: the horizontal cylindrical, or the spherical rotary; or the upright digester. The lye used, in the case of caustic soda, contains 6–8 p.ct. NaOH. After introducing the lye and closing the boiler, the heating is rapidly taken to the maximum steam pressure (90–110 lb.), at which it is maintained for 8–10 hours. The resulting pulp is washed by the process of economic lixiviation in successive tanks, and is obtained of a brownish-grey colour. The dark brown lye is treated for the recovery of the soda by the process of evaporating and calcining.

Sulphate or Sulphide Process.—In this variation of the soda process advantage is taken of the fact that sulphate of soda is reduced to sulphide in the process of evaporating and igniting with the organic matter dissolved from the lignocellulose. In the first instance caustic soda must be added with the sulphate. After boiling with a lye containing 3 parts of the latter to 1 part caustic, evaporating and igniting, an ash is obtained with about 80 p.ct. Na_2O in the form of carbonate, hydrate and sulphide. For a subsequent operation sulphate is added to the amount of about one-third of the total soda compounds, and in a succession of operations the soda lost is made up by additions of sulphate.

The main objection to this process (which is not practised in England) is the formation of organic sulphur compounds of penetrating and objectionable smell. It yields a pulp of excellent quality, for which the coniferous woods are exclusively used as raw materials.

The Sulphite Process.—The introduction and development of this process to its present position of first-rate importance marks an epoch in paper-making. As the alkali processes of treating esparto, etc., mark the period 1850–75, the 'bisulphite wood' industry is a main feature of the period 1875–1900: both adding to the paper-maker's supplies, celluloses of different characteristics from the 'rag' celluloses, chemically inferior, but structurally offering certain advantages in regard to the production of cheap papers.

As already explained, these processes rest primarily on the action of sulphurous acid, which fact was certainly recognised by B. C. Tilghmann, the original inventor of these processes.* At that period, however, the practical manipulation of sulphurous acid of the requisite concentration in aqueous solution (8–12 p.c. SO_2) was a problem yet to be solved. Hence it was that the alternative of the bisulphites was fixed upon by the pioneer inventors named in the historical summary of p. 67; and these processes have, in fact, been developed, to the entire exclusion of the chemically simpler process in which the pure acid is used. This latter process, though practically demonstrated by Prof. Pictet in 1883–86 as having some important advantages, has not been industrially developed.†

In the development of the bisulphite system, the work

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* U.S. Patents 70,485 1867, and 92,229 1869.

† For further information we may refer the reader to a brochure by the authors: 'The Pictet-Brelaz System of Preparing Wood Cellulose.' London, 1887. E. & F. N. Spon.

of Ekman and his associates in the period 1870–80 certainly takes first rank. The later work of Mitscherlich in Germany and Partington in this country contributed largely to the establishment of the industry upon its present colossal scale. It is not, however, within the scope of this work to follow the history of this process in detail. The achievements of successive inventors have been in the perfection of the chemical engineering of the process; whereas its essential features and the character of the pulp have remained very much as they were established twenty years ago.

We may briefly notice some of the more important technical difficulties, the overcoming of which, with the various ways of doing so, really constitutes the history of the development of the manufacture.

Preparation of Bisulphite Liquor.—In practice the bisulphites of lime and magnesia are exclusively used. The source of the sulphur dioxide is sulphur or pyrites. Sulphur 'burning'—the union of sulphur with atmospheric oxygen, according to the simple equation $S + O_2 = SO_2$—is a reaction requiring careful regulation. To supply 1 lb. of oxygen for the combustion of 1 lb. of sulphur, the quantity of air required is 54 cubic feet. Excess of oxygen leads to waste in two directions: the suphurous acid is further oxidised to SO_3, and the temperature of combustion is increased to the point of volatilisation of sulphur.

In absorbing the gas two methods are employed: (*a*) the basic substance in the form of oxide is prepared in a state of fine division and suspension in water, and the sulphur dioxide (diluted with nitrogen) is caused to pass through the liquid mixture; (*b*) the basic substance in the form of carbonate is presented in large masses to the action of the gas, with a regulated stream of water flowing in the opposite direction.

For each of these typical methods a large number of different forms of apparatus have been devised, the common aim being the continuous and automatic production of a liquor of the requisite concentration (total SO_2 p.ct.), and composition (ratio of free SO_2 to SO_2 combined with CaO and MgO) with the minimum waste of SO_2, escaping unabsorbed, and the minimum incidental oxidation to sulphuric acid.

The following is given by Griffin and Little[†] as the composition of a standard bisulphite liquor prepared from dolomite:—

SPECIFIC GRAVITY AT 15°, 1·0582.

	Per cent.			
SO_2 Sulphurous acid	4·41	combine as	Sulphate of lime	0·22
SO_3 Sulphuric acid	0·13		Bisulphite of lime	2·84
CaO Lime	0·95		Bisulphite of magnesia	3·04
MgO Magnesia	0·72		Free sulphurous acid	0·11
SiO_2 Silica	0·02			

Preparation of the Wood.—Unlike the alkali process, which resolves all the compound celluloses, the bisulphite treatment is a specific resolution of the ligno-celluloses; and to attack these uniformly and normally the wood must be freely and rapidly penetrated by the solution. Hence, first, the bark must be completely removed, and the knots of the wood must be dealt with, either by boring out previously to the digestion, or by removal after the boiling.

In addition therefore to breaking up the bark of the wood mechanically (1) by chipping, and (2) by further disintegrating the chips by means of crushing rolls, a careful sorting out of rotten knots and unsound portions precedes the transference to the digestors.

The Digestors.—Apart from variations in form as between cylindrical and spherical rotary boilers, and the stationary upright digestor, the problem of a satisfactory acid-resisting material or lining for the interior of the boilers has been more or less perfectly solved by a large number of inventors. At the outset, lead linings were exclusively used. This metal, in union with an iron shell, involves the effects of the unequal expansion of the two metals under heat, with the result of a 'creeping' of the lining. To minimise this

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[*] 'Chemistry of Paper Making.'

defect, and at the same time to provide adequate support for the 'soft' and heavy metal, many types of construction have been devised. While, however, in the process of evolution a very satisfactory control of these numerous difficulties was arrived at, the lead linings have at this date given way to non-metallic protective coatings, composed of 'cements' of varying composition, and variously applied. The introduction of these linings appears to date from the observations of Brungger in 1883, that an iron pipe temporarily used for the steam supply to a digestor was rapidly coated with a protective scale derived from the bisulphite liquor. Proceeding from this observation, it was found in effect that a plain iron digestor could be provided with such a protective coating by introducing the ordinary bisulphite liquor into the digestor, previously heated by the steam jacket to 110° C. The method was successfully practised for some time, but has again given place to linings of ordinary cement, e.g. a mixture of Portland cement and silicate of soda (Wengel), ground slate and silicate of soda, a mixture of ground slate or glass and Portland cement (Kellner). In other developments a lining of Portland cement is faced with special bricks or tiles, or even slabs of tempered glass.

Boiling Process.—The conditions and duration of the digestion vary somewhat in the different systems of treatment. As an average, about 16–20 hours is required at a pressure of 75 lbs. On the Mitscherlich system a maximum pressure of 45 lbs. obtains, and the time required is much longer, viz. from 70–80 hours. During the process the excess of pressure is relieved from time to time by blowing off, and the sulphurous acid thus escaping is led to one of the 'reaction towers,' in which it is again combined with basic oxides to form fresh liquor.

The Products are of course the pulp, or fibre, and the waste liquor containing the sulphonated lignone bisulphite compounds.

The unbleached fibre, in its washed condition, is still of course an impure cellulose. The following typical analyses are given by Griffin and Little * in illustration of variations in the ordinary market varieties.

—	Mitscherlich Process. Slow Digestion.	Rapid Digestion.			
Moisture	9·000	6·15	6·70	6·57	6·45
Organic matter soluble in dilute acid	0·516	..	..	..	..
Organic matter soluble in dilute alkali	1·505	2·53	2·26	4·25	1·52
Resin	0·060	..	..	..	..
Cellulose	80·800	85·33	89·74	88·12	81·51
Mineral matter (ash)	1·500	1·00	0·45	0·33	0·65
Lignone (by difference)	6·619	5·01	0·85	0·73	9·87
	100·000				

It appears therefore that the better grades of sulphite pulp or half-stuff yield from 85 to 90 p.ct. of 'pure,' i.e. bleached cellulose, each calculated to the same basis of air-dry moisture.

The waste liquor contains the sulphonated lignone compounds, the composition of which we have dealt with on p. 65. The problem of utilising these by-products was investigated by the authors in 1883–5. It was found that they are largely precipitated by gelatin in presence of sulphuric acid or alum, the precipitate agglomerating to a caoutchouc-like mass of greyish colour. The compound thus obtained is soluble in weak alkaline solutions—e.g. solutions of sodium sulphite, phosphate, carbonate — and in this form is available as a sizing material.†

The preparation of the material has been further developed in recent years by Mitscherlich.‡ In engine-sizing paper (see p. 183), the solution is added to the beaker, and the colloidal compound is thrown out of solution by the addition of a

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* Loc. cit., pp. 267–8.

† English Patent, 1548, 1883.

‡ German Patent, 82,498, 1893.

calculated proportion of sulphate of alumina. It contributes in this way to the welding together of the fibres in the machine, i.e. to the 'closing' and toughening of the sheet.

Recent investigations by H. Seidl * have confirmed those of Tollens and of the authors as to the composition and constitution of the dissolved lignone derivatives, and have also resulted in another practical application of these waste liquors, viz. to replace tartar and lactic acid as adjuncts to the process of mordanting wool with soluble chromates.†

Such uses, however, for a by-product produced on an enormous scale, must be regarded as of relatively small importance; and in fact are hardly sufficient to affect their present position as 'waste products'—from which it remains for future researches to rescue them.

Jute, Flax and Hemp, Scutching Waste, Manila, etc.—In addition to the processes above described, all of which are concerned with the production of pure celluloses of the respective classes, and for use in writing and printing papers, a number of raw materials are treated by less drastic methods, producing a purified and disintegrated form of the original raw material, and by no means a pure cellulose. Pulps of this sort are used for the most part in wrapping papers.

The boiling processes already described under Esparto and Straw are, with certain modifications, equally applicable to fibres of this class. For convenience in manipulation they are usually cut into small pieces by a machine such as is shown in Fig. 16, and are then cleaned and dusted in a willowing machine. The boiling process calls for no special notice beyond what has been already said with regard to other fibres.

A cheaper method, and one which is largely adopted in mills which make wrapping and packing papers, consists in

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* Rev. Gen. d. Mat. Col. 1898, pp. 370–3.

† See also Journ. Soc. Chem. Ind. 1898, pp. 923 and 1043; English Patent 19,005, 1897.

boiling the jute or other fibre in lime. Such a treatment is usually not so effective as one in which caustic soda is used, and the fibre produced is harder and coarser in every way. The yield of pulp, however, owing to the fact that the fibre is imperfectly resolved, is greater. In many cases, from questions of economy, lime may be advantageously employed.

Jute and Adansonia are largely used for papers where strength is of more importance than appearance, such, for example, as paper for telegram forms, strong wrapping paper, etc.

Jute—in the form of cuttings or 'butts,' spinners' wastes, and bagging—is usually boiled with lime in cylindrical or spherical rotary digestors. By the use of this base at comparatively low boiling pressures (10–20 lbs.) a well softened half-stuff is obtained, which yields easily to the action of the beaters.

It should be noted, on the other hand, that jute may be fully resolved to a cellulose of very valuable paper-making quality. In this case the treatment required is either (1) a severe treatment with caustic soda, as for the woods, but at somewhat lower pressures (70–90 lbs.) and with less alkali proportioned to its lower percentage of lignone groups; or (2) a relatively light alkaline treatment followed by treatment with chlorine gas and subsequent removal of the products of chlorination by solution in alkaline liquids.

Flax and Hemp Wastes.—In the mechanical processes of separating the flax and hemp fibres, a fibrous waste is produced consisting of the bast fibres themselves, with varying proportions of the wood of the stems. These and the lower grades of spinners' wastes are usually worked up by the paper-maker, *not* for a pure cellulose, but for a half-stuff of less purity and therefore low colour. Various methods of alkaline treatment are adopted, i.e. boiling under pressure with lime or soda, or mixtures of the alkalis. In certain mills the method of chlorination has been practised for the purpose of attacking and resolving the wood. In this case, as in that of jute, the preliminary alkaline treatment may be much 'milder.'

Attention may be called to the industrial problem of working up for paper-making half-stuff the enormous quantities of flax 'straw' which are wasted, in fact burned, in countries where the plant is grown for seed (linseed) only, as in the western states of North America. After separating the seed by thrashing, the 'straw' is not in a condition for treating for a textile fibre. It contains, however, 20–25 p.ct. of such fibre, and by a treatment drastic enough to break down (chemically) the wood and the cuticular celluloses, a 'cellulose' half-stuff is obtained which undoubtedly ranks very high as a paper-making material. The utilisation of flax in this way is again the subject of serious industrial enterprise, and it would appear that the product is destined to become an important staple.

Manila may be taken as the representative of the rope-making fibres, in which group are included the various aloe fibres (Sisal, etc.) and Phormium. The paper-making qualities of manila are sufficiently characteristic to yield papers easily identified by their toughened and parchment-like quality. The fibre comes to the mill chiefly in the form of old ropes. These are cut down by hand and subsequently further disintegrated in machines, in which it is cleansed by dusting. It is then boiled with soda or lime under a varying change of conditions, according as it is required for envelope papers, cartridges, or brown wrappings.

Miscellaneous Raw Materials.—In addition to the staple raw materials which are treated chemically in the paper-mill as above described, there are a large number of fibrous products which fulfil in themselves the requirements of the paper-maker, but which from various causes, such as cost of collecting or transport, are not generally available.

Bamboo.—The numerous species of *Bambusa* furnish a stem which may be broadly characterised as a gigantic straw, and, when resolved by a severe alkaline treatment yields a pulp which has very much in common with th celluloses of our cereal straws. This raw material was thoroughly investigated by Thomas Routledge in the period 1870–5, and many attempts have been made to take advantage permanently of its proved capacities, but the matter remains practically undeveloped.

Mégasse is the name given to the fibrous tissue of the sugar-cane after the extraction of the juice—this cane or stem having a close resemblance to the bamboo. The material has been successfully treated, but the yield of pulp is low, and it is available only for the lowest class of papers.

Adansonia is the fibrous bast or inner bark of the *Adansonia digitata*, a tropical species which grows luxuriantly in the West African forests. It finds a limited use in this country, especially for wrapping papers requiring a very high finish. For this purpose it is boiled with lime. Treated with soda, it may be fully bleached to a cellulose of very valuable paper-making quality.

Sunn Hemp (*Crotalaria juncea*).—This is a useful fibre, and it finds a limited sale in the English market. It is a bast fibre separated from the stem of the plant after a retting process. It has been tested experimentally for paper-making, and for papers of the higher grades, but it has not come into general use.

Rhea, Ramie, China Grass.—These are bast fibres of species of the nettle order. They readily yield, under alkaline treatment (caustic soda), a pure cellulose, and the ultimate fibres are distinguished for their exceptional length. The fibre comes to the paper-maker in the form of spinners' wastes, and is available for papers of the highest grades. It is used to a limited extent for papers of special quality.

'Broke' Paper.—Under this head may be included all the partially formed paper which is always obtained in greater or less degree when a paper-machine is started, or such portions as are occasionally unavoidably damaged in its passage over the drying cylinders, together with the imperfect or rejected portions. It may also include used or waste paper, a large proportion of which, if not too dirty, is remade into paper. The cleaner portions, especially if they have not been dried, are frequently returned direct to the beaters, and mixed with other pulp. That which has been actually made into paper requires to be softened by boiling in water and gentle breaking in an engine. It may be necessary to heat it for a short time in a weak solution of caustic soda. This may be done either in a breaker or in special tanks provided for the purpose. Paper which has been printed upon requires a rather more drastic treatment, and it must of course be used for an inferior quality of paper, as it is impossible to get it to as good a colour as the original pulp from which it was made—at least not economically. 'Broke' paper may be advantageously disintegrated by means of an edge-runner. It consists of a pair of stones arranged in the same way as an ordinary mortar-mill (Fig. 27).

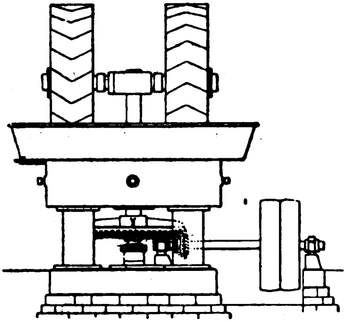

FIG. 27.

Mechanical Wood Pulp.—A very large quantity of pulp is used in the commoner kinds of paper, such as cheap news, etc., which is obtained by disintegrating wood by mechanical means alone, no chemicals being employed. The idea of making paper in this way dates back about 100 years, but owing to the want of suitable machinery it is only lately that a good product has been obtained. The following are, in a general way, the details of the process employed:—

The wood is first cut up into blocks, the size of which is determined by the width of the stones used for grinding; any knots present are cut out with an axe. The stones are made of sandstone, and are covered over three quadrants with an iron casing, the remaining quadrant being exposed. The surfaces of the stones are made rough by the pressure of a steel roll studded with points, and which is pressed against it while revolving. In addition to this, channels about ¼ in. deep are cut into the stone at distances of 2–3 in. They are made in two sets, crossing each other in the centre of the stone, and serve to carry off the pulp to the sides of the stone, in addition to giving increased grinding-surface. The pressure of the blocks of wood against the stones is steadily maintained by screws worked by suitable gearing; this is necessary in order to obtain a pulp of uniform character. A stream of water is kept constantly playing on the stone; by this means the pulp, as fast as it is formed, can be conveniently carried away. It is first passed through a rake, which retains small pieces of wood that have escaped grinding. The stream of pulp then passes through the sorters, the object of which is to keep back such portions of the wood as have not been sufficiently disintegrated. These consist of cylinders about 3 ft. long and 2 ft. in diameter, covered with a coarse wire-cloth. The fibres that are retained by this wire fall into the refiners, which consist of a couple of horizontal cylinders of sandstone, the upper one only of which revolves. Here they are further disintegrated, and are again passed through the wire-cloth; this is repeated until all the fibres have passed through. The pulp, after passing through the first sorter, may be conducted through a series of gradually increasing fineness, and, by this means, be separated into different qualities. Though pulp so prepared cannot compare with chemically-prepared stuff, as the fibres are extremely short and have comparatively little felting-power, it may be used with advantage as a sort of filling material.

Various modifications of the foregoing process have from time to time been proposed. Among others, that of softening the wood by previous soaking in water, or steaming, proves to be valuable, as by so doing it is found that a longer fibre can be obtained, the soft wood being more readily torn away by the stones. Some inventors have proposed

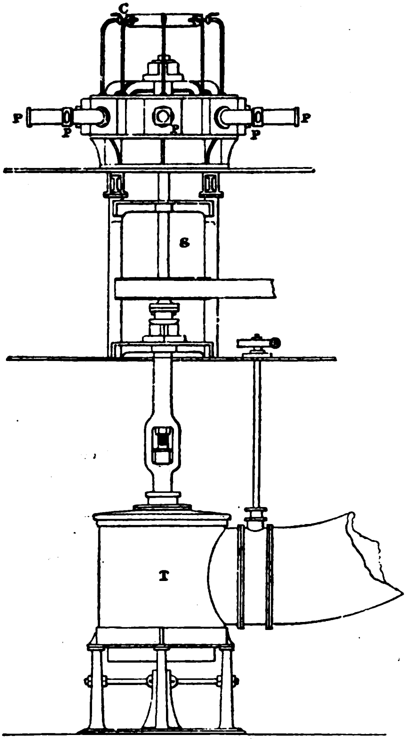

FIG. 28.

to replace the sandstone by an artificial stone containing a large quantity of emery.

An improved method of preparing mechanical wood pulp lately patented by Mr. A. L. Thune, of Christiania, has been communicated to us by Mr. Carl Christensen.

The apparatus employed is shown in Figs. 28, 29, and 30. Fig. 28 illustrates an arrangement of grinding apparatus fixed direct on to a turbine. The stone is fastened on to the shaft S worked by the turbine T. The wood in the form of small blocks is kept in contact with the stone by a number of hydraulic presses P.

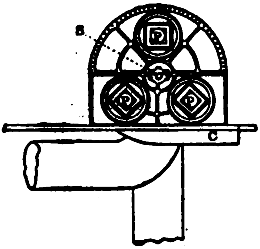

FIG. 29.

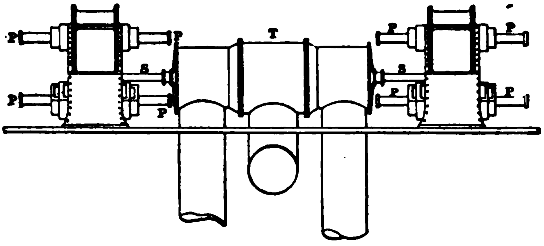

FIG. 30.

A somewhat similar arrangement, but placed horizontally, is shown in front and side elevations in Figs. 29 and 30. The same letters correspond.

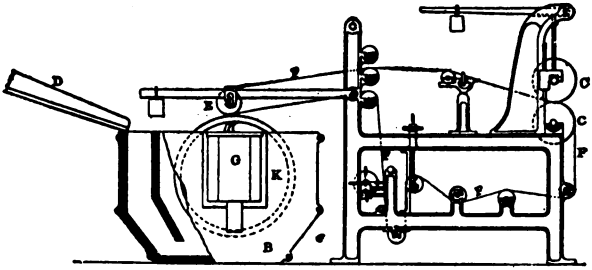

FIG. 31.

The ground and sorted pulp is made into thick sheets by means of the board machine shown in Fig. 31. The pulp mixed with water passes down the shoot D into the vat B in which the cylinder K revolves. This cylinder is covered with wire-cloth, and as it revolves it takes with it a certain quantity of pulp in the form of a continuous sheet.

This sheet is taken on to the endless travelling felt F by the small couch roll E. When it reaches the rolls C C it is wound round the upper one, from which it is removed when a sufficient thickness is obtained. Obtained in this form the pulp is readily transported.

The woods commonly employed are white pine and aspen. The latter yields a pulp of a better colour, but of inferior strength than the former.

Paper containing mechanical wood pulp is very liable to become discoloured by the action of air and light, the lignocelluloses being much more readily acted upon than the celluloses isolated from them. Such fibre is, moreover, devoid of much felting power; it has, in fact, little to recommend it but its comparative cheapness. It is nevertheless used in large quantities, some cheap papers being made almost entirely from it.

In reference to the alkaline treatment of fibres dealt with in the early part of this chapter, a Table of Strength of Caustic Soda Solution will be found useful for reference, for which see the next page.

TABLE OF STRENGTH OF CAUSTIC SODA SOLUTIONS (15° C. = 59° F.) (TÜNNERMAN).

Specific Gravity.	Degrees Twaddle.[*]	Per cent. Na_2O.	Equivalent Percentage of 60 per cent. Caustic Soda.
1·0040	0·80	0·302	0·503
1·0081	1·62	0·601	1·001
1·0163	3·26	1·209	2·015
1·0246	4·92	1·813	3·021
1·0330	6 60	2·418	4·030
1·0414	8·28	3·022	5·037
1·0500	10·00	3·626	6·043
1·0587	11·74	4·231	7·051
1·0675	13·50	4·835	8·059
1·0764	15·28	5·440	9·067
1·0855	17·10	6·044	10·073
1·0948	18·96	6·648	11·080
1·1042	20·84	7·253	12·090
1·1137	22·74	7·857	13·095
1·1233	24·66	8·462	14·103
1·1330	26·60	9·066	15·110
1·1428	28·56	9·670	16·117
1·1528	30·56	10·275	17·125
1·1630	32·60	10·879	18·131
1·1734	34·68	11·484	19·140
1·1841	36·82	12·088	20·147
1·1948	38·96	12·692	21·153
1·2058	41·16	13·297	22·161
1·2178	43·56	13·901	23·170
1·2280	45·60	14·506	24·177
1·2392	47·84	15·110	25·170

NOTE.—It must be borne in mind that the above numbers refer only to solutions of pure caustic soda. With liquors containing sodium chloride, sulphate, etc., the specific gravity will give an erroneous view of the amount of alkali present, as these salts of course raise the gravity. For example, a liquor prepared by causticising a solution of recovered soda has a specific gravity of 1·05 (10° Tw.). According to the above table, this corresponds to 6·043 per cent. of 60 per cent. caustic. Tested by means of standard acid it showed 4·520 per cent. Too much reliance should therefore not be placed upon determinations of specific gravity, but in important cases the actual amount of alkali should be determined by titration with standard acid.

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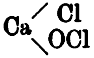
[*] To convert degrees Twaddle into specific gravity, multiply by 5, add 1000, and divide by 1000; thus, 7° Tw.,

7 × 5 = 35
1000
1000) 1035 (1·035 sp. gr.
1000
3500
3000
5000
5000

CHAPTER VI.

BLEACHING.

THE bleaching of the pulp or half-stuff resulting from the chemical treatment of the various raw materials, is the second stage in the purification of the cellulose or compound cellulose; in the former case the residues of non-cellulose constituents are entirely removed, in the latter the product is more or less 'whitened,' but a considerable proportion of the non-cellulose constituents survive the process and consequently the pulp remains coloured more or less. The 'chemical' wood pulps, it may be mentioned, are largely used in the unbleached condition; the 'sulphite' pulps are usually of a pinkish-grey colour, and they are used directly in 'toned' or greyish-white papers. The 'mechanical' wood pulps, for reasons which will appear, are used almost universally without any bleaching treatment, and they give a greyish tone to the lowest grades of 'printings,' of which they are the main constituent.

Paper-makers' bleaches are essentially processes of oxidation. The agents employed are alkaline compounds of certain acid, oxidising oxides, and the alkalis contribute to the effect by hydrolysing the coloured compounds present in the fibre to be bleached, and by combining with the colourless products of the oxidation. Though several oxidising or bleaching agents are available, the use of 'bleaching powder' so enormously preponderates, that it is the only method we need consider in any detail. Bleaching powder, commonly known as 'chloride of lime,' is prepared by the action of chlorine gas upon slaked lime, the latter absorbing more than half its weight of the gas. The resulting compound is usually formulated as  $Ca\begin{smallmatrix}/Cl\\ \backslash OCl\end{smallmatrix}$; but when treated with water the compound is hydrolysed and resolved into equal molecules of calcium chloride, $CaCl_2$, and *Calcium Hypochlorite*, $Ca(OCl)_2$, the latter being the active oxidising or bleaching compound. The hypochlorites are the salts of the acid HClO, which is the hydrate of the oxide Cl_2O, thus:

$$Cl_2O + H_2O = 2HClO.$$

It must be noted also that the resulting hypochlorous acid decomposes in acting as an oxidant into HCl + O, and therefore the oxide Cl_2O is equivalent in oxidising action to O_2, and *vice versâ*, the O_2 obtained from bleaching powder represents $2Cl_2$, and as the active constituent of these bleaching solutions is always expressed in terms of *Chlorine*, it is now clear that the apparent loss of half the active chlorine, as the inert $CaCl_2$, which attends the act of solution in water, is only a change of terms, viz. to oxygen. In this sense, therefore, and in regard to oxidising actions, the whole of the chlorine of a normal bleaching powder is 'available chlorine.'

For the actual composition of a normal bleaching powder we cite an analysis by Griffin and Little:—*

Available chlorine	37·00	Total Cl 37·60
Chlorine as chloride	0·35	
Chlorine as chlorate	0·25	
Lime	44·49	
Magnesia	0·40	
Silicious matter	0·40	
Oxides of iron, alumina and manganese	0·48	
Carbonic acid	0·18	
Water and loss	16·45	
	100·00	

This analysis is one of a series, the purpose of which was to determine the rate of depreciation of bleaching powder when stored in the usual hard wood cakes at temperatures

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* 'Chemistry of Paper Making,' p. 278.

not exceeding 62° F. At the expiration of eleven months the 'chlorine' numbers of the above had changed to—

Available chlorine	33·80
Chlorine as chloride	2·44
Chlorine as chlorate	0·00

During the same period the carbonic acid had increased from 0·18 to 0·80.

It is to be remembered, therefore, that bleaching powder is an unstable compound, and the supplies should be stored in dry, cool places, and out of the range of any possible contact with products of combustion, i.e. of coal or coal-gas.

Preparation of the Solution.—The solution is best prepared in a vessel provided with stirrers or agitators, whereby a thorough mixture of the bleaching powder and water is obtained. Bleaching powder always contains a certain amount of free lime and calcium carbonate, which remain undissolved as a residue which should be allowed to settle to the bottom of the vessel, and the clear liquor run off. The residue may then be again treated with water, or with weak liquor obtained in a previous operation. If the washings are too weak to be conveniently used for bleaching, they may be stored in a separate tank and used for dissolving fresh powder. In this way a strong stock solution can be readily prepared, the powder at the same time being thoroughly exhausted. The washing should be repeated as frequently as possible, after which the residue may be allowed to drain. This operation is best conducted on a filter-bed provided with an air-pump similar to that described in Chapter XI. The residue is obtained in this way as a hard cake, containing about 60 p.ct. of water. If the above operations have been properly conducted, it should not contain more than about 0·25 p.ct. of chlorine. It is, as above stated, mainly composed of lime, i.e. the hydrated oxide of calcium $Ca(OH)_2$, and carbonate of lime. Calculated on the dry substance, the former amounts to about 60 p.ct. and the latter to 30 p.ct.

The original powder should contain from 33·0 to 37·0 p.ct. of 'available chlorine,' that is, chlorine which is effective in the bleaching process.

If possible, one or more large store tanks should be provided for the strong bleach liquor, so that time may be given for the complete separation of the insoluble portions. The liquor can be drawn off with a 'siphon' pipe without disturbing the residue.

It is generally advisable that only clear liquor be used, as a milky solution of calcium hypochlorite is much more sluggish in its action than one which is perfectly clear and bright.

A convenient strength for the stock solution is 6° Twaddle: this corresponds to about half a pound of bleaching powder to the gallon.

The solution of the hypochlorite is also liable to deterioration with loss of 'chlorine' strength. It must, therefore, be stored in cool places, and there should be a minimum of exposure to the atmosphere. This is secured by storing in relatively deep vessels.

The following reactions of the hypochlorites and their practical bearings are important:—

1. They liberate iodine from the iodides. Free iodine gives a deep indigo blue coloration with starch. Hence the usual test solution for the presence of these compounds, viz. a starch paste containing potassium iodide.

Test Papers are made by soaking pure cellulose (filter) papers in the mixture and rapidly drying in a pure atmosphere. Care must be taken to avoid oxidation of the iodide to iodate, as a mixture of these salts is decomposed by the weakest acids with liberation of iodine, thus—

$$5KI + KIO_3 + 6HCl = 6KCl + 3H_2O + 3I_2.$$

In using the test papers with acid solutions the test papers should be themselves tested with a weak acid (acetic).

2. In adding the hypochlorites to a soluble iodide in presence of acid, the following reaction takes place:—

$$Cl_2O = 2HClO + 4HI = 2HCl + 2H_2O + 2I_2.$$

In this case both the chlorine and oxygen are converted into the joint equivalent of free halogen. The reaction affords a rapid and satisfactory analytical method, i.e. for estimating 'available Cl.'

3. The hypochlorites are instantly 'destroyed' by hydrogen peroxide, thus—

$$NaClO + H_2O_2 = NaCl + H_2O + O_2\,;$$

that is with production of entirely 'neutral' compounds. In estimating the alkalinity or acidity of a bleaching liquor the hypochlorite is destroyed by a neutral solution of the peroxide; after which ordinary indicators may be used, and the products titrated with acid or alkali to the neutral point.

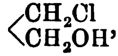
4. The neutral sulphites are oxidised to the neutral sulphates:

$$Na_2SO_3 + NaClO = Na_2SO_4 + NaCl.$$

Both the above reactions are useful therefore in 'neutralising' or destroying excess of 'bleach.'

5. 'Organic' or carbon compounds react with the hypochlorites in various ways; (*a*) they are simply *oxidised*, thus—

$$\underset{\text{Aldehyde}}{K\cdot COH} + NaClO = \underset{\text{Acid}}{K\cdot COOH} + NaCl.$$

(*b*) they are *chlorinated* in various ways; thus, saturated compounds, such as alcohol, acetone, aldehyde, yield *chloroform* (CCl_3H): unsaturated compounds may yield chlorhydrins, $CH_2\cdot CH_2 + ClOH =$  $\left\langle\begin{matrix}CH_2Cl\\CH_2OH\end{matrix}\right.$, or if aromatic derivatives, chlorinated phenols, quinones, etc. Also it must be remembered that strong hydrochloric acid liberates *chlorine* from the hypochlorites; a large number of acids set free the hypochlorous acid, which however is very unstable and readily decomposes with liberation of chlorine. Thus the lignocelluloses are very liable to *chlorination* under treatment with bleaching powder solution, as a result of the secondary reactions. In bleaching jute (half-bleach) or wood pulps (cellulose bleach) a basic reaction should be maintained throughout. The presence of chlorinated lignone compounds is shown by the colour reaction with sodium sulphite (p. 54).

The method of testing the powder and its solution will be described in Chapter XIII.

Bleaching Process.—The washed and broken pulp is placed in the 'potcher,' together with the necessary quantity of bleaching liquor and as much water as is required to produce complete circulation of the mass. In many mills the breaker itself answers the purpose of a potcher also. The quantity of water should be kept as low as possible, as it is found that by the use of strong solutions less bleaching powder is required than with weak solutions; moreover, less time is required to produce the effect. On the other hand, with very strong solutions, the pulp is liable to be injuriously affected.

Straw and esparto pulps are sometimes bleached in large potchers made of brick covered with cement. The circulation of the pulp is produced by the action of paddles made of wood or, preferably, of iron.

Many 'potchers' are provided with steam pipes, whereby the mass of pulp and liquor is heated. This should be done with great care, so as to avoid superheating in any part, as this is certain to cause destruction of the fibre. The better plan, where it can be adopted, is to uniformly heat the pulp before running in the bleach.

In certain cases the action of the calcium hypochlorite is assisted and accelerated by the addition of either sulphuric or hydrochloric acids; these combine with the lime and liberate hypochlorous acid, which has a more rapid action than its calcium salt. If the acid be added in too large quantity or of too great a strength, it sometimes happens that instead of hypochlorous acid chlorine gas is given off, part of which escapes into the air, thus causing loss. Moreover, the chlorine is liable to enter into combination with the fibre-substance, forming the yellow chlorination products described on p. 55.

This liability is greater in the case of highly lignified fibres, such as wood or jute: in these cases, therefore, the use of acids should be avoided. When used the acid should be largely diluted with water and added gradually. The best plan is to allow the action of the bleach to continue for some time, only adding the acid when it is nearly exhausted. In this way risk of damage to the pulp is avoided.

The diluted acid should be conveyed by a leaden pipe passing down to the floor of the potcher, and perforated at its lower extremity.

In bleaching half-stuff from flax waste or new linen pieces, i.e. rags, after the alkali boil, the acid bleach is useful in resolving the residues of lignocellulose or 'sheave.' The treatment is in the case of rags usually carried out in a 'tumbler' or revolving barrel made of wood, and suitably lined internally with resistant material. The barrel is charged through a manhole and, after the liquor is added, set in circulation. After some time the acid is added through the manhole and the circulation continued.

Other means of accelerating the action of the bleaching powder have been suggested, such, for example, as the use of bicarbonate of soda, which by double decomposition forms with the bleaching powder carbonate of lime and free hypochlorous acid. It is, however, much too expensive an agent.

The amount of bleaching powder necessary to produce a good white colour differs materially with the fibre to be bleached, and of course with the degree of resolution of the fibre-substance in the preliminary treatment with caustic soda.

The following numbers may be taken to be approximations of the amount necessary to bleach well-boiled pulps:—

	Per cent. Powder, calculated on Original Fibre.
Rags	2 to 5
Esparto	7 „ 12
Straw	7 „ 10
Wood	15 „ 20

A well-boiled pulp should contain from 90 to 95 p.ct. of cellulose, that is, in other words, will lose from 5 to 10 p.ct. in weight in the process of bleaching.

Very excellent results are sometimes obtained by substituting sodium or magnesium hypochlorite for the calcium compound. This is done by decomposing a solution of bleaching powder with an equivalent quantity of either sodium sulphate or carbonate, or magnesium sulphate. The precipitate of calcium sulphate or carbonate is allowed to settle, and the clear liquor run off. The soda solution is more sluggish in its action than one of calcium hypochlorite, but it is more easily controlled, and is less liable to injure any material treated with it. From a comparative study by the authors, of the bleaching actions of these three hypochlorites;* it appears that the chemical reactions are simplest in presence of magnesia, this base favouring *oxidation*; with lime as base there is a greater tendency to *chlorination*; soda is intermediate.

The time necessary to produce a perfect bleach depends on the nature and condition of the pulp, on the degree of concentration of the liquor, and on the temperature at which the operation is conducted. Some paper-makers prefer to extend the bleaching over a considerable period of time, but this involves the employment of a larger system of 'potchers,' which in many instances is an objection. If this method is adopted, especially in the case of straw or esparto, the action of the paddles or roll should be stopped, as otherwise the fibres are liable to felt together in the form

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* Journ. Soc. Chem. Ind., 1890.

of small grains, which sometimes escape the action of the beating roll, and occasionally find their way into the paper, causing an unevenness of surface. By giving longer time to the bleaching there is less risk of damage to the fibre, and consequently a greater yield of bleached pulp.

The action of the bleaching solution should, as far as possible, be confined to the non-cellulose portions of the fibre. A certain action on the cellulose itself invariably takes place, but it should be reduced to a minimum. The action of bleach upon cellulose has been indicated in Chapter I., p. 42. For further information on this subject the reader is referred to the 'Journal of the Society of Chemical Industry,' 1884, April 29 and May 29.

A very good method of bleaching consists in a preliminary treatment in the ordinary way in the potcher, followed by a prolonged steeping in tanks.

In the case of pulps which are very difficult to bleach, the action can be greatly assisted by washing out the products of the bleaching action, treating the pulp for a short time with a weak alkaline solution, again washing, and then repeating the bleaching process. In this way very refractory pulps can easily be bleached. Even an intermediate washing with water is useful. Such refractory pulps are sometimes obtained in the bisulphite-wood process. Griffin and Little * have put on record a careful investigation of such a case where the difficulty of bleaching was traced to an impurity of an organic sulphur compound. With an intermediate alkaline treatment the usual high colour was obtained.

In most cases, where a fairly good colour has been obtained by the use of bleaching powder alone, the colour is greatly improved by a souring or treatment with weak hydrochloric acid, or, better still, with solution of sulphurous acid.

Or the bleaching may be conducted in two or more operations with intermediate treatments with acid.

All these modifications, however, are more or less trouble-

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* 'Chemistry of Paper Making,' pp. 287, 288.

some, and should only be resorted to when the ordinary method fails.

After bleaching, a certain quantity of hypochlorite, i.e. 'active chlorine,' always remains in the pulp. It may be removed in the potcher itself, or when the pulp reaches the beater. In any case, the methods adopted are the same. (See p. 183.)

In some mills it is the practice to free the bleached pulp from the soluble by-products of the bleaching process by pressing the pulp in hydraulic presses, or by draining in vats provided with perforated bottoms. Or the pulp may be made to pass through a pulp-saver.

In modern practice the presse-pâte system is more generally adopted: this is, for evident reasons, the most thorough method of finally purifying the cellulose.

Chlorine gas as a bleaching agent has been almost entirely superseded by the more manageable calcium hypochlorite. Its employment is open to the serious objection indicated before, viz. the liability to form difficultly removable chlorine compounds. Its use as a disintegrating agent has already been alluded to (see p. 136).

The introduction of liquefied chlorine, however, reopens the question of the practical application of the halogen itself. For information on this matter see 'Annalen der Chemie,' 259, p. 100 (R. Kneitsch).

A process has been suggested and patented (English patent No. 11,333, 1884), by Prof. Lunge, which involves the use of acetic acid. The quantity required is, however, very small, as during the process of bleaching it becomes regenerated. The free lime in the bleaching powder solution should first be nearly neutralised with a cheaper acid, such as hydrochloric or sulphuric, followed then by the addition of the acetic acid. This process, we are informed, gives excellent results with high-class material, such as the best cotton and linen rags; it is, however, not to be recommended for such materials as the straw or esparto, or wood cellulose, nor for the jute half-bleaches.

For the bleaching of rags the process invented by Thompson (English patent No. 595, 1883) has also proved effective. The method consists in saturating the material with a weak solution of bleaching powder, and then exposing them to the action of carbonic acid gas, alternating the treatment with liquor and gas until the bleaching is complete. In this way the bleaching action is made very rapid and effective.

Electrolytic Bleaching.—Various attempts have from time to time been made to bleach by means of electricity—that is to say, by means of the products of the electrolysis of solutions of alkaline chlorides and the chlorides of the alkaline earths. The first process to be industrially developed was that of M. Hermite. This process is based upon the electrolysis of a solution of magnesium chloride, this salt having been found to give the most economical results. The solution, at a strength of about 2·5 per cent. of the anhydrous salt ($MgCl_2$), is electrolysed until it contains the equivalent of about 3·0 grms. chlorine per litre. This solution is then run into the 'potcher' containing the pulp to be bleached; a continuous stream is then kept up, the excess being removed by means of a drum-washer. This excess, which after being in contact with the pulp in the engine is more or less deprived of its bleaching properties, is then returned to the electrolysing vat, where it is again brought up to the normal strength.

The electrolysing vat consists of a rectangular vessel of slate or other suitable material. The negative electrode may be constructed of zinc; for the positive it is necessary to employ platinum. Each electrolyte contains a large number of pairs of plates disposed in series, the electrical connection being of course 'in parallel.'

The electrolysed solution has been found to possess very remarkable properties, which have considerable bearing upon the economy of the process. If a solution be taken of equal oxidising efficiency with one of calcium hypochlorite, as indicated by the arsenious acid test (see p. 279), it is found that the former possesses greater *bleaching* efficiency than the latter in the proportion of 5 to 3. Moreover, the bleaching is much more rapid, and the loss of weight which the substances undergo is less, for equal degrees of whiteness obtained.

It has been shown that by the electrolytic method the bleaching of paper pulp can be effected at much less cost than with bleaching powder. The process has been extensively employed in French mills.

It must be noted here that the 'Hermite' system was originally based upon a continuous circulation of the bleaching liquid in between the potcher and electrolyser. This however, is only practicable in the case of rag celluloses; in bleaching esparto and wood the organic matter dissolved in the bleaching liquid leads to many inconveniences, such as frothing and to a serious loss of current by short-circuiting and by doing waste work (oxidation) on the dissolved organic matter.

Consequently this and other electrolytic systems have resolved themselves very much into the preparation of a bleaching solution, which is then run into the potcher and used in the same manner as a solution of bleaching powder.

Although this is a considerable practical simplification, it involves a certain sacrifice of 'bleaching efficiency.' It still appears, however, that the electrolytic solutions show a certain economy when compared with solutions of bleaching powder.

In estimating the relative costs, the following are the essential data for arriving at the cost of the 'electrolytic chlorine.'

(1) *The unit of quantity* of current is the ampère; one ampère per hour in passing through the electrolyte solution 'liberating' its 'equivalent' of 1·3 grm. chlorine at the anode, and the corresponding quantity of sodium at the kathode.

The above are the electro-chemical equivalents, i.e. theoretical numbers; in practice the yield is considerably less than the theoretical, as in this kind of electrolysis there are complications due to secondary reactions. The unit of current must therefore be taken as yielding 70–80 p.ct. of the equivalent of 'available' or hypochlorite chlorine, say 1 ampère = 1 grm. of active chlorine.

2. *The resistance* against which the current has to be forced is measured in units known as *volts*: in this order of processes a 'pressure' of 3–4 volts is required between the terminals. The product (ampères and volts) is the energy or work expended: and this is expressed in the same units as mechanical work—of which 746 go to the 'horse-power.'

Hence we have the following cycle of related quantities:

2 lbs. of coal by combustion and steam raising are converted into a horse-power of mechanical energy, which exerted through one hour amounts to 746 'watts': this is converted through the dynamo, with attendant loss, into say, 630 similar units of electrical work.

To liberate 1000 grms. of chlorine we require 1000 ampères, which, at 3·5 volts, consume 3500 units of energy, i.e. require a force of 5–6 horse-power per hour.*

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* Journ. Soc. Chem. Ind. 1892, p. 963.

CHAPTER VII.

BEATING.

THE bleached pulp is still in the condition of 'half-stuff,' requiring a further and final treatment. If it were attempted to make paper from the pulp in the state in which it leaves the 'potchers' or 'steeping' chests, it would be found to be wanting in evenness of texture and other qualities which mark a well-made sheet of paper. This result is only secured by a process of disintegration and comminution, the main and immediate purpose of which is the complete separation of the individual fibres, which in the half-stuff still adhere to one another and are more or less agglomerated into masses. At the same time also it is necessary for the uniformity of the stuff that the fibres should be more or less reduced in length, which is accomplished partly by cutting, partly by drawing out or shredding the fibres. These are in effect the more important mechanical results of the beating process.

The machines or beaters in which this process is carried out resemble in general appearance the breaking engines previously described; the roll, however, carries more knives, and it is usually let down much nearer to the bed-plate. In the case of fibrous substances, whose ultimate fibres are relatively short (see table, p. 88), it is only necessary to split up the filaments into their constituent fibres: esparto, straw, and wood are of this class. In the case of straw, the disintegration is for the most part accomplished in the boiling and bleaching processes, and therefore but little work devolves upon the beater. Esparto and wood require a certain amount of beating, but this should be regulated to the drawing asunder of the individual fibres, the cutting of the fibres being carefully restricted. This is accomplished by adjusting the distance of the roll from the bed-plate, so that by the friction of the fibres upon themselves, when passing over the plate, a kind of rubbing or 'brushing' is produced. If a carefully-made paper of esparto or wood be examined by the microscope, it will be found that the majority of the fibres preserve the pointed or slightly rounded ends characteristic of the bast or wood cells. On the other hand, it is obvious that cotton, whose ultimate fibres have a length of 20 to 40 mm., and flax (25–30 mm.), with other similar fibres, will require to be broken up into short fragments in order to develop to the fullest the 'felting' property of the pulp. Not only are the fibres reduced to the most favourable dimensions, but in cotton and linen a further contributory advantage accrues; for on account of the internal structure of the ultimate fibres they tend to split up at the point of rupture into a number of fibrillæ, which, in the case of cotton, take the form of a network; and in case of linen, are seen as a bundle of distinct fibres parallel to and continuous with the fibre. This gives the ends of the fragments a ragged contour, which has considerable influence on the felting power of the pulp, and therefore on the strength of the paper into which it is made.

With these fibres, therefore, the 'cutting' as distinguished from the 'breaking' action should be avoided as much as possible, otherwise the effect described above will not be produced, and the fibres will show instead a clean cut. The appearance shown by cotton and linen pulp, when thoroughly 'beaten' and ready to be made into paper, is given in the frontispiece, which is taken from the authors' micro-photographs.

The 'half-stuff' is furnished to the 'beater,' or 'beating' engine as it is sometimes called, previously partially filled with water. The furnishing is done in successive portions, the first being allowed to mix thoroughly with the water before another lot is added. This is continued until the mass or 'furnish' is of a certain consistence, depending upon the nature of the pulp and the character of the paper to be made. In perhaps the majority of cases the aim is to work the furnish as stiff or thick as is consistent with free circulation in the beater under the action of the roll. Owing to the construction of the beater, it frequently happens that a portion of the pulp lodges in the corners, from which the beater-man removes it by means of a wooden paddle, which also serves to push forward the pulp to the roll in case the motion is inclined to be sluggish. The proportion of water to pulp should not be too high, otherwise the beating is not so effective; at the same time, if the mass is allowed to get too thick, imperfect circulation results.

The operation of 'beating' occupies a considerable time, and consumes a large amount of power. Cotton and linen rags naturally take longer—in some cases as much as ten hours is given to the operation, and the time is further prolonged in the case of stuff required for exceptionally thin paper, e.g. tissues.

Esparto, on the other hand, can be sufficiently disintegrated in from two to four hours.

Wood pulp requires very gentle beating; it is therefore necessary to prolong the time to about six hours.

These differences in the duration and method of beating should be borne in mind when pulps of different natures are mixed together in the same beater, as is frequently the case. It is better, with very dissimilar fibres, to 'beat' each separately, and only to mix them in the stuff-chests. This, however, is open to the objection that the pulps may be insufficiently mixed.

The length of fibre to which pulps should be reduced depends to some extent upon the kind of paper to which it is to be applied. The authors have examined a number of papers by well-known makers, and find the dimensions in millimetres of various pulps to be as follows:—

Fibre.	Maximum.	Minimum.	Mean.
Cotton	1·32	0·23	0·75
Linen	1·20	0·20	0·76
Esparto	1·40	0·40	1·00
Straw	1·50	0·50	0·88
Wood	2·60	1·00	2·00

Wood and straw pulp, when imported in the form of dry sheets, may, before being beaten, be conveniently disintegrated and thoroughly mixed with water by means of the edge-runner described under 'Broke' Paper, p. 147, Fig. 27.

There is a certain quality in beaten stuff, as compared with the original half-stuff, usually expressed by such adjective terms as 'wet' or 'greasy,' which has an important influence upon the working of the stuff upon the machine, and therefore directly affects the quality of the finished paper. This effect is largely the result of the beating process, but is essentially influenced by the special characteristics of the celluloses themselves—that is, by their respective capacity for taking up water with production of gelatinous hydrates. The differentiation of the celluloses in this respect has been previously dealt with. The effects contributed by the beating operation will be best appreciated by reference to an extreme case. When a cellulose half-stuff is beaten for a prolonged period (40–150 hours) its condition approximates to that of the homogeneous, structureless, gelatinous mass, which is obtained by the spontaneous 'setting' of dilute solutions of the sulpho-carbonates (p. 23). Moreover, on draining and drying, the cellulose compacts itself to masses which can be shaped by moulding and turning. The structural material obtained in this way has been termed *cellulith.* It is sufficiently obvious that a proportion of cellulose in this form enables the stuff to hold more water in its passage over the wire-cloth of the machine, and contributes in the later stages of the making to the welding of the fibres together, and to the closing and compacting of the sheet of paper. It is also obvious that the proportion converted into this form or modification varies directly with the duration of the beating. Moreover, in this regard, there is no substitute for time, and since to attain this quality in the stuff is an important function of the beating, we must recognise a limit to increased efficiency of beaters as measured by reduction of time. The claim of advantage of sizing with solutions of cellulose, on the other hand, rests upon the instantaneous production by this means of the effects of long beating.

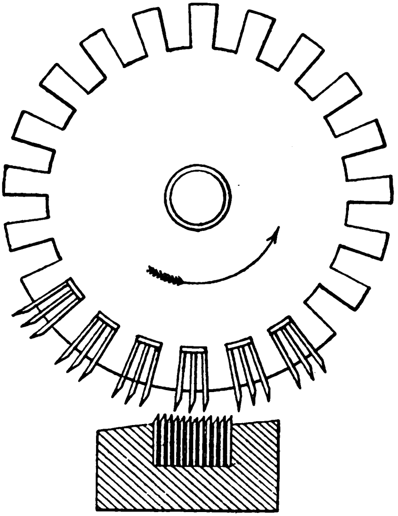

FIG. 32.

In making the finer kinds of paper, the roller bars or knives, instead of being made of steel, are made of bronze; thus any contamination with oxide of iron is avoided. This is especially liable to take place in case of steel knives when the beater has been allowed to stand for some time.

The inside of the beater itself is often lined with lead, a material which is not liable to oxidise, and which can very readily be cleaned.

When a beater has been running for some time, the knives of the roll and the bed-plate become worn and so far reduced that they must be taken out and re-cut. The bed-plate is removed, firmly fixed in the bed of a planing machine, and the edges trimmed by means of a chisel, so as to cut the knives at the proper angle.

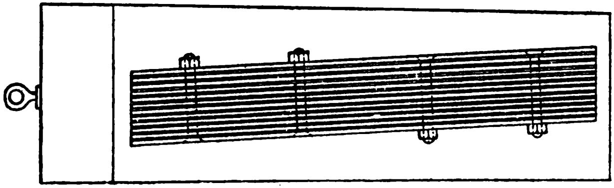

Fig. 33.

The roll and bed-plate are shown in section in Fig. 32. Fig. 33 is a plan of a bed-plate, and Fig. 34 illustrates the manner in which the knives are fixed.

It will be seen that the knives in the bed-plate are placed so that they do not lie parallel with those of the roll. This arrangement imitates to some extent the action of a pair of scissors. Occasionally the knives are slightly bent, so as to form a very obtuse angle. Bed-plates so fitted are called 'knee-plates.' They are largely used in America, but not much in this country.

To obviate the necessity of removing the roll, a small machine has been devised whereby the knives can be cut *in situ.* This machine, which can be firmly fixed between the

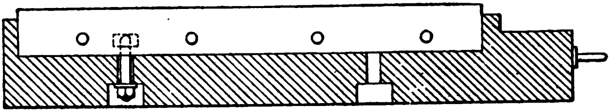

Fig. 34.

mid-feather and the side of the beater, consists of a small steam-engine which actuates a movable cutter, made to pass to and fro horizontally along the edge of each knife in succession. The engine is supplied with steam by a piece of strong flexible rubber tubing.

The ordinary form of beater is fitted with a single roll, and the general arrangement of its working parts is that already described and figured, p. 119, for a 'breaking' engine. This type of beater is known as the Hollander. Its main defects in working are those of imperfect circulation of the stuff. They are largely obviated by certain additions and modifications of structure embodied in 'Tait's Patent Beating Hollander.' The essential modification consists in heightening the back fall, with the introduction of a guard, concentric with the roll, thus forming a narrow passage for the passage of the stuff, ensuring its continued circulation and preventing its falling back on the roll. By avoiding this local churning action, the entire contents of the beater passes more frequently through and under the roll. The structural improvements in question are indicated in the shaded portions of the accompanying sectional sketch.

Tait's improvements to the ordinary Hollander cannot be better described than in terms of the inventors' patent specification :—*

'The object of this invention is in an engine provided with a guide or fence to guide or direct the pulp away from the back of the roll and prevent the pulp from being carried round with and over the top of the roll.

'According to this invention a passage is formed at the back of the roll and so placed that the pulp is forced or thrown through this passage into the trough of the engine and prevented from being carried round with the roll.

'In an engine constructed according to this invention, the passage through which the pulp is thrown into the trough may be formed at any point behind the dead-plate.

'In existing engines the passage may be formed by raising

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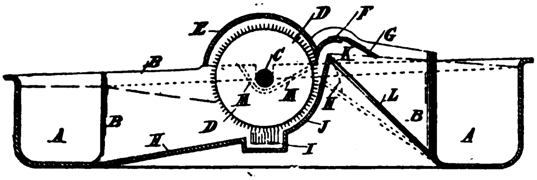
* English patent 23,130, 1892. Thomas Tait and John Hood.

the backfall and giving it a suitable shape by means of a block of wood, iron or cement fixing to the cover or sides of the engine a guide or doctor extending the whole width of the roll, so as to form a passage of a suitable shape between the raised backfall and guide through which the pulp is thrown or directed away from the roll and into the trough of the engine.

Fig. 35.



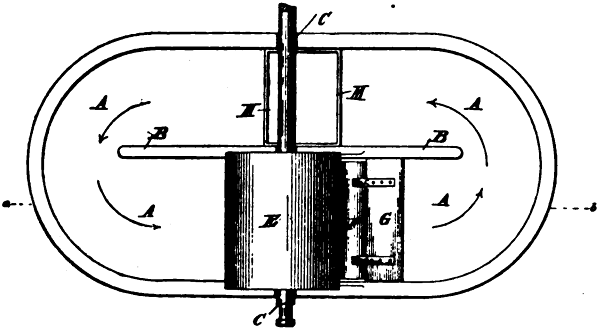


Fig. 36.

'The annexed drawings show our invention.

'Fig. 35 is a section on the line *a b* of Fig. 36, which is a plan of the beater engine.

'A is the trough, B the partition therein, C is the shaft and D the beater roll, E is the shield with a curved guide F, from which is hung by hinges a flap G. H is the uprising incline of the bottom to the dead-plate I, the bottom then being curved at J to the neck K, from which is the descent-plate or backfall L. This may be at any angle such as is indicated by full lines, the dotted lines showing the height at which the backfall of an existing beater engine is carried; the additional height can be made to form the narrow passage by building up on the existing one by a lump such as that shown by the curved dotted line N. M is the guard in the open return part of the trough A and under the shaft C.

'The space between the top edge of the backfall L and of shield E and guide F is of such shape and narrow, but of the full width of the roll E to prevent the 'stuff' falling back between the roll E, curved plate J, or of being carried round by the roll E, whereby the stuff has a better travel and circulation than usual, and passes oftener and more regularly between the roll and the plate.

'By this invention the stuff is more freely delivered behind the roll and stands higher in the trough than in ordinary beater engines, and the guard not only protects the shaft, but enables the stuff to move uniformly along the return side of the trough."

The inventors claim as the special points of novelty—(1) utilising the centrifugal force imparted to the 'stuff' (by the roll E) by taking it through a narrow opening from the roll to the trough. This arrangement, together with (2) the shape of the backfall and guide, producing a better circulation of the stuff and an increase of beating action in a given time.

Certain new forms of beaters have lately been introduced in this country, and are rapidly gaining in favour, chiefly on account of the saving of driving power, and the space occupied, compared with the amount of 'stuff' they are capable of beating.

The *Acme beater* (Bertram & Shand's patent) embodies original features, in construction and working of which the more essential are (1) the elevation of the beating roll from the main pulp channel; (2) the provision of a screw propeller

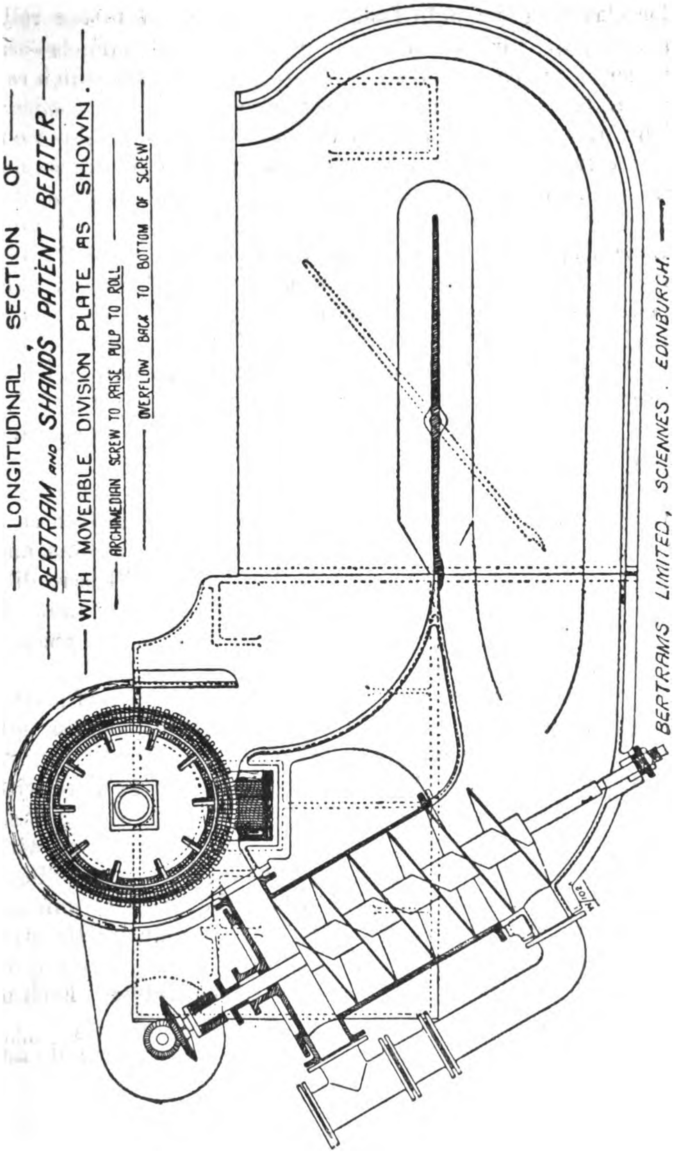

LONGITUDINAL SECTION OF
BERTRAM AND SHAND'S PATENT BEATER
WITH MOVEABLE DIVISION PLATE AS SHOWN.
ARCHIMEDIAN SCREW TO RAISE PULP TO ROLL
OVERFLOW BACK TO BOTTOM OF SCREW
W/102
BERTRAMS LIMITED, SCIENNES, EDINBURGH.

FIG. 37.

for elevating the pulp from the main channel to the roll; and (3) the division of the trough into two channels—the upper of which contains the roll—by a partition which can be made to swing in a practically perpendicular position. This arrangement simplifies the emptying and washing out of the engine. These more important particulars are set out in the annexed figure (Fig. 37), which represents a longitudinal section of the beater. We are indebted to the firm of Bertrams, Limited, of Edinburgh, the makers of this beater, for the drawing, and for information respecting this and other machines; and we take this opportunity of advising our readers of the important 'Illustrated Catalogue of Paper Mill Machinery,' published by this firm, which will be found to contain a complete descriptive account of the paper machine and all auxiliary appliances, in their most improved and modernised forms.

The Refining or Perfecting Engine is a more modern development of the beater. It may be shortly described as a 'concentrated beater.' The working of such a machine, and the principles of treatment which it embodies, will be readily grasped from the annexed illustrations of the 'Marshall Engine,' Fig. 38, showing the working parts of the engine, and Fig. 39 the engine in elevation.*

The stuff is taken from the beater in a condition of partial preparation, and is further triturated in its passage through the engine, which consists of the two essential parts: A, a cast-iron cone revolving within the fixed cone A′, fitted with steel angled knives, and B a cast-iron disc revolving at an adjusted distance from the stationary disc B′, also fitted with angled knives held in position by hard wood wedges or fillets. The work of the former is to reduce the fibres to uniform length, the disc portion of the engine then reducing the stuff in the plane at right angles, that is by breaking up fibre-aggregates or even splitting the fibres themselves. Each of

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* We are indebted to Messrs. Bentley and Jackson, Bury, Lancashire, for these illustrations of the Marshall engine, of which they are the sole makers for Europe.

these parts having, moreover, a separate adjustment, the work of the engine may be thrown on the one or the other, according to the requirements of the stuff and of the quality of the paper to be made. It is claimed for this engine that it effects a considerable economy in the time of beating, in addition to the advantages resulting from a more uniform preparation of the stuff. It must be remembered, however, that in paper-making, as in the processes incidental to the preparation of textile materials, there are effects which time only can produce, and that therefore the refining engine is at the best only capable of substituting the work of the ordinary beating roll within limits.

In Umpherston's patent engine great economy of space is effected by causing the pulp to travel over and under the backfall (*a*, Fig. 40). Another advantage is that the stuff circulates freely with less water than in the ordinary forms,

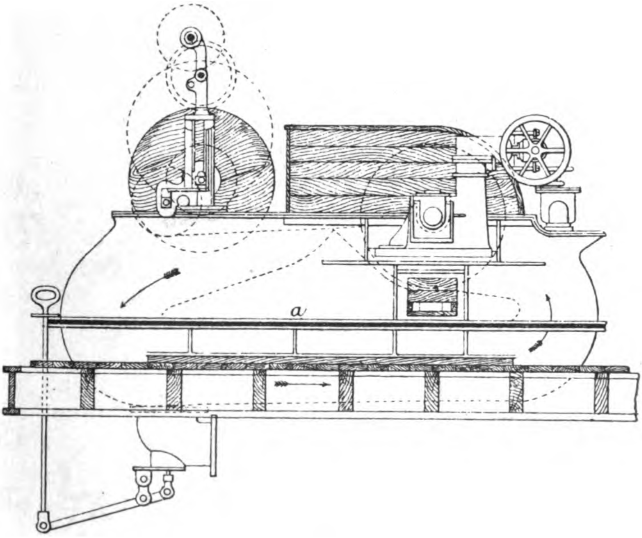

FIG. 40.

thus increasing its output. It is also claimed that the pulp is beaten with less power, and, as it is less liable to lodge in corners, it is more evenly beaten.

The construction of the engine will be readily understood by reference to Fig. 40. The direction which the stuff takes is indicated by the arrows.

The quality of the water used to furnish the engine is a matter of very great importance, especially in the manufacture of high-class papers. Above all it should be free from suspended matter, and from dissolved iron; the former finds its way directly into the paper, and the latter is liable to become precipitated in the pulp as oxide, thus injuriously affecting its colour. Careful settling and filtration are sufficient to eliminate insoluble matter; soluble impurities are more difficult of removal; therefore the water should, if possible, be free from them. In most mills settling ponds are provided for the purpose of removing suspended matter, and in addition it is usual to employ woollen filter-bags fastened to the nozzle of the pipe that supplies the beaters with water.

For methods of purifying water see p. 285.

Driving of Beating Engines.—Without treating in detail the question of the transmission of power from the main engine of the mill, we may note that at this date the most approved method is to drive by means of rope pulleys; the rope driving being adopted both as between the steam engine and the shafting supplying the power to the beaters, and also in transmitting power from this shafting to each beater. Cotton ropes are to be preferred; usually a rope is composed of five principal strands. Such an installation is found to transmit power with the least amount of shocks and strains, and incidental repairs can be carried out at convenient intervals for shutting down, i.e. with the minimum of disturbance of the mechanical routine of the mill.

CHAPTER VIII.

SIZING, LOADING, COLOURING, ETC.

We have now to describe various auxiliary preparations which are carried out in the beater, each contributing some important quality to the finished sheet of paper.

Excepting in mills where the pulp after bleaching is treated on the press-pâte, the bleached half-stuff as furnished to the beater often contains an excess of bleaching compounds, which can be removed in two ways, viz. by washing or by decomposition with an 'antichlor.' The first method has the advantage of not only removing the bleach, but of also eliminating the chloride of calcium, partly existing ready formed, and also that resulting from the decomposition of the calcium hypochlorite originally present in the bleach. On the other hand, this method takes some time, and consumes a large amount of water, which in some mills is a matter of considerable importance. Where practised, the beaters are provided with one or more drum-washers (see Fig. 36). An additional objection to this method lies in the fact that a certain quantity of fibre passes through the meshes of the wire-cloth covering the washers, and is thus lost.

The more usual plan is to remove the residual bleach by decomposing it with an 'antichlor.' A substance frequently employed for this purpose is sodium thiosulphate, which, in presence of calcium hypochlorite, is oxidised to sodium sulphate, with formation of calcium chloride. Double decomposition then takes place between these salts, with formation of calcium sulphate and sodium chloride. The reactions which take place may be expressed by the following equation:—

$$\underset{\substack{\text{Calcium}\\ \text{hypochlorite.}}}{2(Ca(ClO)_2)} + \underset{\substack{\text{Sodium}\\ \text{thiosulphate.}}}{Na_2S_2O_3} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Calcium}\\ \text{sulphate.}}}{2CaSO_4} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{2HCl} + \underset{\substack{\text{Sodium}\\ \text{chloride.}}}{2NaCl}.$$

The above decomposition does not accurately represent the action of bleach upon sodium thiosulphate. If the solutions employed are highly dilute, the decomposition may take place in another direction, viz.:—

$$\underset{\substack{\text{Calcium}\\ \text{hypochlorite.}}}{Ca(ClO)_2} + \underset{\substack{\text{Sodium}\\ \text{thiosulphate.}}}{4\ Na_2S_2O_3} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Sodium}\\ \text{tetrathionate.}}}{2\ Na_2S_4O_6} + \underset{\substack{\text{Sodium}\\ \text{chloride.}}}{2\ NaCl}$$

$$+ \underset{\text{Caustic soda.}}{2\ NaOH} + \underset{\text{Lime.}}{CaO}.$$

At the particular degree of dilution which occurs in a beater, the bleach is decomposed almost entirely according to the first of the equations; from which, on calculating, it will be seen that 158 parts of sodium thiosulphate are equivalent to 286 parts of calcium hypochlorite. As commercial sodium thiosulphate contains 36·3 p.ct. of water, and bleaching powder 70 p.ct. of calcium hypochlorite, on the basis of 35 p.ct. available chlorine, it follows that 248 parts of the former are required to neutralise 409 parts of the latter.

Within the last few years other forms of 'antichlor' have been introduced, such, for example, as the various sulphites. The most important of these is sodium sulphite, which, in its ordinary crystallised form contains 50 p.ct. of the actual sulphite, as may be calculated from the formula of the salt $Na_2So_37H_2O$. More concentrated forms are prepared by the action of sulphurous acid upon soda ash. It is obvious also that calcium and magnesium sulphites may be used to replace the more expensive sodium salt.

Sulphites are converted by the action of bleach into sulphates, thus:—

$$\underset{\substack{\text{Calcium}\\ \text{hypochlorite.}}}{Ca(OCl)_2} + \underset{\substack{\text{Sodium}\\ \text{sulphite.}}}{2Na_2SO_3} = \underset{\substack{\text{Calcium}\\ \text{sulphate.}}}{CaSO_4} + \underset{\substack{\text{Sodium}\\ \text{sulphate.}}}{Na_2SO_4} + \underset{\substack{\text{Sodium}\\ \text{chloride.}}}{2NaCl}.$$

From this equation it will be seen that 252 parts of sodium sulphite will neutralise 143 parts of calcium hypochlorite, or 204·3 parts of bleaching powder. Assuming that crystallised sodium sulphite contains 50 p.ct. Na_2SO_3, the same amount of bleach would require 504 parts. Comparing these numbers with those given above for sodium hyposulphite, it will be seen that 204·5 parts of bleach require for neutralisation 129 parts of sodium thiosulphate and 504 parts of crystallised sodium sulphite, or proportionately less of stronger products.

Sodium sulphite is preferred to sodium thiosulphate by most paper-makers, notwithstanding the fact that even in its most concentrated form nearly three times as much is required to produce a certain result. It is found that when it is used the wire-cloth of the machine is preserved for a longer time than if sodium thiosulphate is employed. This may be due to the fact that with the latter a certain amount of free acid is always formed, which of course would act injuriously on the wire; whereas, when sodium sulphite is used, the products of decomposition are neutral salts without any action upon metals. (See the above equations.)

Hydrogen peroxide has been used to some extent as an 'antichlor' with satisfactory results. The only objection to its use is its relatively high cost.

Whichever variety of 'antichlor' is used, an excess should be carefully avoided, as all act more or less upon the size and colouring matter added to the pulp subsequently. The quantity is easily adjusted, either by an actual estimation of the 'chlorine' in the pulp and calculating therefrom, or the 'antichlor' may be added gradually, testing the stuff from time to time with the iodide test papers (p. 156).

Sizing.—If the celluloses, reduced by the beating process to the condition of ultimate fibres, or further disintegrated by tearing and cutting to 'artificial' units of suitable length, are put together into a sheet or web, the product will be a 'blotting' or bibulous paper. Such papers have a well known use; and 'blottings' are in effect made from cellulose pulps with the addition of a small proportion of starch, added to the beater in the form of starch paste, and for the purpose of adding a certain 'binding' quality to the fibres. Such papers, in addition to their absorbent properties for liquids, are 'soft,' relatively weak, and altogether unsuited to uses involving mechanical wear and tear.

Writing papers on the other hand have, as is well known, a totally different texture and 'handle,' and they have a certain water and ink-resisting quality: that is, they are required to oppose as little resistance as possible to the mechanical action of writing, but to resist the penetration of the ink in such a way that the written characters sink into the substance of the paper in the one direction only, i.e. at right angles to the surface.

These properties are in large part *added* by means of *sizing agents.* While we shall consider the sizing process from this point of view, it must not be forgotten that the texture of the paper is an important factor, and that this is influenced by everything which tends to 'close' the sheet: for instance, the mineral loading agents (to be dealt with in the next section) have the effect of filling up the interspaces between the fibres: or the effect may be produced by suitable beating of the pulp. Thus, though the 'sizing' of paper may appear to be a simple process of adding substances of certain water-resisting quality, which quality they communicate to the paper, the experienced paper-maker recognises it as a really complicated result, influenced by a great number of factors. This is more particularly the case with the pulp or engine-sizing processes—which, in the sequence of treatments will be considered here. The alternative method of sizing the finished sheet or web, 'tub-sizing,' as it is called, is a simpler process which in the case of machine-made papers is carried out on the paper-machine, and will be dealt with in that connection.

Engine sizing. (Rosin-alum-sizing)—For the specific water- or ink-resisting quality specially required in writing and wrapping papers, we are practically limited to rosin or colophony. This well-known substance is the residue from turpentine distillation. It consists of an acid body, abietic acid ($C_{44}H_{64}O_5$), or rather of its anhydride ($C_{44}H_{62}O_4$). By virtue of its acid character and the solubility of the sodium salt ($C_{44}H_{62}O_5Na_2$) of the acid, rosin is rapidly dissolved on heating with solutions of the alkalis, e.g. carbonate of soda, caustic soda. The solution of the rosin-soap is similar in properties to solutions of the ordinary soaps, which are soda compounds of the higher fatty acids, and in fact the similarity of properties is such that mixtures of fat and resin acids, the latter in large proportion, are the basis of the 'yellow' soaps of commerce, which, outside the slight difference in colour and smell, are not distinguishable from fatty acid soaps.

The reaction between abietic acid and carbonate of soda, with expulsion of carbonic acid (gas), may be formulated as follows :—

$$\underset{[672]}{C_{44}H_{64}O_5} + \underset{[106]}{Na_2CO_3} = C_{44}H_{62}O_5, Na_2 + CO_2 + \underset{[\text{Beilstein}]}{H_2O} ;$$

that is, 100 parts of the pure acid require 15·7 of the pure carbonate to form, with the sodium oxide which it contains, the 'neutral' resinate. Commercial rosin being a mixture, and containing other acids which require more soda per unit, and, on the other hand, hydrocarbons and some other compounds devoid of acid properties, the 'equivalent' of soda (carbonate) will vary from 15 to 18 p.ct. with various rosins. The equivalent is readily determined for any sample by warming with excess of a standard solution of caustic soda in alcohol till completely dissolved, and titrating the excess of soda with a standard alcoholic acid in presence of phenol phtalein, as indicated (see p. 282.)

To make the *neutral* rosin size on the large scale, the calculated quantity of soda ash is dissolved in about twelve times its weight of water, heated preferably in a jacketed pan: the rosin, previously crushed, is gradually added to about six times the weight of the ash, and the boiling continued 3–4 hours until a perfect solution results.

The frothing due to the escape of large quantities of carbonic acid is controlled by the form of the boiling vessel, and by limiting the steam jacket to the lower portion, so that the sides are not superheated.

The boiling being finished, the strong 'size' is run off into iron tanks, where in cooling and standing a separation of the 'pure' soda-resinate takes place as a semi-solid mass surrounded by a dark coloured liquor, which is a solution of various by-products.

In the older practice of size-making this solution was drained away and the size again boiled up with water. On cooling a further separation of coloured products takes place, with a consequent further purification of the 'size.' These operations requiring considerable time, it was customary to boil the supply of size many days in advance, the interval being required for the series of cleansing operations. The quantity of this size per 100 lbs. paper is that representing 3–4 lbs. of the original rosin.

In later practice, however, a rosin size is largely used, differing from the above in containing 15 to 25 p.ct. of rosin over and above the 'equivalent' of the soda, the excess of rosin being dissolved in the strong size in the free or uncombined state. For an *acid size* of this composition, finishing with 25 p.ct. of 'free rosin,' the following formula is given by C. Beadle:—170 lbs. soda ash in 200 gallons of water are boiled with gradual addition of 1300 lb. rosin; the boiling is continued 7 hours, and the volume finally made up to 225 gallons. The acid size on dilution gives a milky liquid, due to suspension of the 'free' rosin in a finely divided condition. More care is required in diluting the size preparatory to adding to the beater, since with undissolved rosin there is a danger of agglomeration to particles of such dimensions as would cause rosin-specks in the paper. The danger is lessened by adding starch to the diluting water. The following working formula is given by Wurster (*infra*):—In a suitable vessel water is heated to 50° C. A quantity of starch calculated to 15–20 p.ct. of the rosin in the size to be diluted, is stirred with warm water to a cream and added to the vessel, which is then heated to 80° until the starch is entirely 'dissolved.' The temperature is lowered to 50–60° by adding water, and the strong size is then stirred in. Finally the temperature is gradually raised to 65°. The extent of dilution has a considerable effect on the efficiency of the size. Wurster recommends a 3 p.ct. limit, i.e. 3 lbs. rosin per 10 gallons size.

The quantity of the acid size usually required is that representing 2–3 lb. of the original rosin per 100 lb. paper.

The sizing operation consists, *first*, in adding the size, prepared by either of the above methods, to the pulp in the beater, passing it through a fine sieve or a coarse cloth filter-bag. It is usually added when the pulp is one-half or two-thirds beaten. But following the addition of the size is a *second* operation by which the decomposition of the soda-resinate is determined, or perhaps rather completed, and the resin acids fixed upon the pulp in the insoluble condition. The reagent used for this purpose, almost universally, is alum or sulphate of alumina. In elucidating this reaction we must consider some of the properties of the alkali salts of the resin and fatty acids. These salts are easily decomposed by the weak acids, even carbonic acid, the action of which, expressed by the equation

$$CO_2 + H_2O + C_{44}H_{62}O_5.\ Na_2 = Na_2CO_3 + C_{44}H_{64}O_5,$$

is the exact reverse of that formulated on p. 185, and it takes place in dilute solution at the ordinary temperature. We note also that 44 parts of carbonic acid (CO_2) set free 682 parts of the resin acid. Other acids act similarly, and in proportion to their equivalents. Such acids, when combined with metallic bases, also pass over to the soda of the resinate when the two salts are brought together in aqueous solution, with simultaneous formation of the resinate of the metallic base. Thus, with calcium salts,

$$\underset{\text{Calcium Chloride.}}{CaCl_2} + Na_2R = Ca \,.\, \underset{R\,=\,\text{Resin Acid.}}{R} + 2\,NaCl\,;$$

$$\underset{\text{Calcium Sulphate.}}{CaSO_4} + Na_2R = Ca \,.\, R + Na_2SO_4.$$

Those reactions are all of practical significance: (1) because nearly all natural waters contain carbonic acid, and many contain the sulphate of lime; and (2) calcium chloride is contributed to the pulp by the bleaching solution, and is present in the beater, less or more, according to the degree of washing of the pulp after bleaching. These resinates are curdy insoluble precipitates. Sulphate of alumina reacts according to the equation—

$$3\,.\,Na_2R + Al_2\,.\,3SO_4 = 3Na_2SO_4 + Al_2R_3\,;$$

i.e. for 3 mol. abietic acid (= 2016) in a *neutral size*, we require 342·8 of the *sulphate*; or in terms of alum, which contains 36·1 p.ct. sulphate of alumina, 949 parts. In the acid sizes, the proportion of soda being less, and in the sulphates of alumina of commerce, the proportion of Al_23SO_4 varying from 40 to 60 p.ct., it is necessary in every mill to construct a table of 'alum' equivalents for the size, according to the composition of each. Thus, as an example, the size is made with 15 p.ct. soda ash per 100 lbs. rosin, and the sulphate of alumina to be used contains 50 p.ct. Al_23SO_4. The 'alum equivalent' per 100 lbs. rosin is

$$\frac{342 \cdot 8}{2} \div 106 \times 15 = 23 \text{ lbs.},$$

or 0·23 sulphate per 1 lb. rosin.

As a matter of fact, however, the quantity used in practice is much in excess of this proportion—usually about three times, but often very much more. This 'optimum' proportion has been determined rather by experience than by quantitative calculations based upon scientific grounds.

In 1878, C. Wurster published a treatise on the Rosin-Alum Sizing Process,* which may be regarded as the first attempt to reduce the process to a scientific or exact basis. Wurster combats the then current view that the actual sizing agent is a resinate of alumina formed as above represented. It appears that ordinary engine-sized papers treated with ether and other solvents of the *resin acids*, entirely lose their water-resisting quality, losing in weight from 2 to 5 p.ct.; these dissolved sizing components are isolated by evaporation of the solvent, and found to be almost entirely composed of the *free rosin acids*. This observation is also confirmed by determining the alumina in the paper before and after extraction; which is found to be but slightly affected. On these results Wurster concludes that the free rosin acids are the effective sizing agents, and hence his advocacy of the acid sizes with a maximum proportion of free or uncombined rosin; hence also the function of the excess of alum, i.e. to decompose the neutral resinate of alumina with liberation of the free acid, thus:—

$$Al_2R_3 + 2(Al_2\,SO_4)_3 + 3\,H_2O = \underset{\text{Free Resin Acid.}}{3\,R\,.\,H_2} + \underset{\text{Basic Sulphate of Alumina.}}{Al_2(Al_2O_3)\,3\,(SO_4).}$$

These views require complementing by a careful consideration of the chemical function of the *cellulose itself*. It is well known that cellulose takes up alumina from solutions of the sulphate and chloride; still more easily from the acetate. It is therefore more than probable that cellulose would decompose the neutral resinate by combining with the alumina. It must also be borne in mind that cellulose contains OH-groups of basic function, and that these would combine simultaneously with the rosin acids; nor is this view negatived by the fact that ether and other solvents dissolve away the rosin acids from the finished paper.

On the whole, therefore, it is to be recommended that

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* 'Le Collage des Papiers,' Bull. Soc. Ind. Mulhouse, 1878, pp. 726-801.

all these contributing factors should be borne in mind: (1) the consumption of alum by the basic constituents of the cellulose half-stuff and of the water used in furnishing; (2) the calculated proportion referred to the soda used in the particular type of rosin size adopted; (3) the proportion required by the cellulose itself. For a further discussion of this somewhat complicated problem, see 'Society of Arts Journal' (Cantor Lectures), Feb. 22, 1897.

Auxiliary Sizing Agents.—Under this heading we may mention certain colloidal substances which are or may be used in the engine-sizing process, chiefly for the purpose of closing and compacting the web of fibres. Two of these we have already had occasion to introduce to notice, viz. *Starch* and *Alumina.*

Starch is used by many makers in large proportion, especially in papers heavily 'loaded' with china clay (p. 200). It is sometimes added in the form of transparent starch paste, prepared by swelling and dissolving the starch at 80–90°; it is a common practice also to boil the clay with its complement of starch. In many mills, again, the starch is added in the raw or unswollen state, the granules become imprisoned in the network of fibres, and are swollen and burst under the heat of the drying cylinders.

Alumina is precipitated as a gelatinous hydrate by the interaction of the soda of the rosin size with sulphate of alumina. Passing through the intermediate form of 'resinate,' it is no doubt finally fixed as the oxide, and aids in cementing the fibres together and filling the interspaces. Both the alumina and starch also aid in keeping the rosin acids in the state of minute subdivision during the beating and making processes.

Cellulose Hydrates (*'Viscose' Sizing*).—In the earlier part of this work attention has been called to the specific characteristics of the celluloses of parenchymatous or 'cellular' as distinguished from fibrous tissue. Under chemical treatment these are gelatinised to hydrated forms which retain a relatively large percentage of water. Such forms of cellulose no doubt play an important part in paper-making. Certainly the special characteristics of straw cellulose are largely due to the presence of such 'cellular' celluloses, and also to the general capacity for hydration of its constituent celluloses. The various solutions of cellulose dealt with in Chapter I. would appear to be available for a similar purpose, but for practical use they are mostly precluded by cost of production.

The sulpho-carbonates, however, being prepared at relatively low cost, and readily decomposed with regeneration of a normal cellulose endowed with powerful cementing properties, are successfully used in engine sizing. The solution, which goes by the name of 'viscose,' is added to the beater in the earlier stages of the beating, and when thoroughly mixed the decomposing salt is added. The salts best adapted to this purpose are the sulphates of zinc and magnesium, the proportion required being calculated to the equivalent of the soda present in the viscose. Thus, as an example, the wood celluloses are converted into 'viscose' with a proportion of caustic soda (NaOH) equal to 40 p.ct. of the weight of the cellulose. The molecular weight of NaOH being 40, and its equivalent of the salts being respectively

$$\frac{ZnSO_4\cdot 7H_2O = 287}{2}, \text{ i.e. } 143\cdot 5$$

and

$$\frac{MgSO_4\cdot 7H_2O = 246}{2}, \text{ i.e. } 123\cdot 0,$$

each lb. of dissolved cellulose will require nearly 1½ lb. of the zinc and 1¼ lb. of the magnesium salt.

The decomposition of the viscose has the effect of coating the fibres with a film of gelatinous cellulose, which exerts a powerful cementing action in the subsequent processes of making and drying, the effects reaching a maximum when the paper is 'loft dried,' i.e. dried in the air without heat. By viscose sizing the contents of the beater are still left in the basic condition, and it is necessary to add alum in slight excess in order to facilitate the working on the machine. The quantity of viscose used is usually from 1 to 5 p.ct. (calculated as dissolved cellulose) of the weight of the paper. The effects produced are a considerable increase of tensile strength and resistance to the action of water, though the sizing in the latter respect is not of the character of rosin sizing. To produce the quality of resistance to penetration by water and ink the addition of rosin is necessary. It is found, however, that very much less of the latter is required, viz. from $\frac{1}{2}$ to $\frac{1}{3}$ the usual quantity, or 1 to 2 p.ct. on the paper. These advantages of the viscose- or cellulose-sizing are realised at only a small additional cost to that of the ordinary plan; but certain disadvantages have to be reckoned with, resulting from the introduction of alkaline sulphur compounds into the beater. These, by interaction with the fibre constituents, and also by action upon iron compounds unavoidably present, cause a certain lowering of colour; and although the sulphur introduced is for the most part eliminated (as CS_2) by the special action of the decomposing salts, and the alkalinity is of course easily neutralised by alum, there is a residual permanent discoloration sufficiently marked to prevent the process being used in the ordinary production of white papers.

Aluminate of Soda has been used to a certain extent as a sizing agent in conjunction with the rosin-soap. Hydrated alumina dissolves in caustic soda by virtue of its acid function—a characteristic which it is important to bear in mind in considering the probable chemical condition of the oxide in the finished paper. The alumina is precipitated from its alkaline solution by the weakest acids, e.g. carbonic acid—and therefore a *à fortiori* by alum itself. It has been proposed to use the aluminate of soda as the solvent for the rosin; but it is difficult to see any advantage resulting from the practice.

The addition of hydrated alumina to the neutral rosin size, during the later stages of the boiling, is rather to be recommended.

Silicate of Soda.—Silica, or SiO_2, is a solid body of weakly acid properties which is precipitated from solutions of its alkaline salts on the addition of acids and acid salts. It takes the form of a gelatinous hydrate which, when formed in the beater, enables the pulp to carry more water in the machine, and produces a hardening effect on the paper. In using this compound the more 'acid' silicates should be selected, e.g. the silicates of formula $Na_2O.2SiO_2$, $Na_2O.3SiO_2$.

Gelatin is little used in engine sizing. Used in this way it fails to give results proportional to cost. Its compound with the sulphonated lignone derivatives, the by-products of the bisulphite processes, has been already mentioned. It is soluble in weak alkaline solutions, in which form it is added to the beater, and on being decomposed with the equivalent of alum is reprecipitated as a tough caoutchouc-like mass, which, as a coating upon the fibres, produces a considerable toughening effect upon the paper.

Casein.—This albuminoid substance, obtained from milk—of which it constitutes nearly 5 p.ct. by weight—is largely used as a sizing agent in the coating of papers. Its use in the engine depends upon the fact that it can be added in the form of a strong solution, from which it is completely precipitated by alum. It imparts toughness and a good 'handle' to the finished paper. Its use is limited by cost, which at present rates is between *4d.* and *5d.* per lb., a cost considerably above the selling price of the bulk of ordinary papers.

Particulars of Materials used in Sizing.

The following are the more important points which determine the value of the materials, their preferential selection, mode of use, etc.

Soda (carbonate) occurs commercially in various forms :—

Crystal Soda $(\underset{106}{Na_2CO_3}\underset{180}{10H_2O})$ is the ordinary 'washing soda.' The crystalline form is a guarantee of purity. From the formula it is seen to contain $\frac{106}{286} \times 100 = 37$ p.ct. only of the carbonate, the remainder being water. It is therefore a relatively costly form of soda to handle.

Crystal Monohydrate ($Na_2CO_3 . H_2O$) was introduced many years ago by Messrs. Gaskell, Deacon & Co. It has one point of advantage over the anhydrous carbonate or soda ash, viz. that it dissolves readily without tending to aggregate to lumps.

Soda Ash (Na_2CO_3, anhydrous and nearly pure).—Before the introduction of the Solvay process and the so-called 'ammonia' soda, soda ash was an impure form of the carbonate. The degree of impurity was such that the percentage of carbonate in the ordinary forms varied from 83 to 90. Such products were objectionable for use in the making of size. Now, however, we have in the aforesaid 'ammonia' soda a remarkably pure product, the percentage of carbonate amounting to 97–98. This answers all requirements for size making.

Solutions of Sodium Carbonate.

SPECIFIC GRAVITIES OF SOLUTIONS OF SODIUM CARBONATE,

At 60° F. = 15° C.

Degrees Twad. 1° = 0·005 Sp. Gr.	Percentage by Weight.		Degrees Twad. 1° = 0·005 Sp. Gr.	Percentage by Weight.	
	Na_2O.	Na_2CO_3.		Na_2O.	Na_2CO_3.
1	0·28	0·47	16	4·42	7·57
2	0·56	0·95	17	4·70	8·04
3	0·84	1·42	18	4·97	8·51
4	1·11	1·90	19	5·24	8·97
5	1·39	2·38	20	5·52	9·43
6	1·67	2·85	21	5·79	9·90
7	1·95	3·33	22	6·06	10·37
8	2·22	3·80	23	6·33	10·83
9	2·50	4·28	24	6·61	11·30
10	2·78	4·76	25	6·88	11·76
11	3·06	5·23	26	7·15	12·23
12	3·34	5·71	27	7·42	12·70
13	3·61	6·17	28	7·70	13·16
14	3·83	6·64	29	7·97	13·63
15	4·16	7·10	30	8·24	14·09

Alum: *Sulphate of Alumina.*—The basis of the alums is the ***normal aluminium sulphate*** $Al_2 3SO_4$; the pûre sulphate is acid to litmus.

Solutions of Aluminic Sulphate.[*]—The solubility of the anhydrous sulphate ($Al_2 . 3 . SO_4$) in water has been determined as follows:—

Temperature 0° C.	0°	10°	20°	30°	45°	50°
100 parts water dissolve of $Al_2 . 3 . SO_4$	31·3	33·5	36·2	40·4	45·7	52·1

The following are the specific gravities at 15° of solutions of varying concentration:—

Per cent. $Al_2 . 3 . SO_4$ ..	5	10	15	20	25
Specific gravity	1·0569	1·1071	1·1574	1·2074	1·2572

Crystal Alum ($Al_2 . K_2 . 4SO_4 + 24H_2O$) is a double salt of aluminium and potassium sulphates, the latter being inert and serving only for procuring a ready crystallisation of the sulphate of alumina. Of this, the 'active' sulphate, the double salt contains 36·1 p.ct. The double salt may be regarded as a pure but diluted form of sulphate of alumina. It is still used in certain mills, but is for the most part superseded by the 'alum cakes.'

The following is a table of strengths of alum solution at 17° C.:—

Percentage of $Al_2K_2(SO_4)_4 . 24H_2O$.	Specific Gravity.	Degrees Twad.
1	1·0065	1·3
2	1·0110	2·2
3	1·0166	3·3
4	1·0218	4·4
5	1·0269	5·4
6	1·0320	6·4

Alum Cakes.—Many years ago an aluminous cake or 'concentrated alum' was introduced into the English paper made by Messrs. Pochin. Such products have now almost entirely displaced the crystal alums. They are made by the action of sulphuric acid upon bauxite or iron-free clays.

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[*] Dic. Chem. Sol., A. M. Coney. London, 1896, Macmillan.

The subjoined analyses of commercial products show the standard of purity which they now maintain:—

Alumina (Al_2O_3)	14·84	14·70	14·95	14·85	16·00	16·20
Ferric oxide (Fe_2O_3)	·06	·12	·05	trace	nil	trace
Sulphuric acid (SO_3)	35·00	34·60	36·09	34·94	38·00	38·00
Free sulphuric acid	·32	·40	nil	·29	nil	nil
Lime (CaO)	·11	·11	·17	·14	·16	·14
Water	49·42	49·95	48·72	49·60	45·50	45·43
	99·75	99·88	99·98	99·82	99·66	99·77

These forms of the sulphate of alumina have this advantage over the crystal alums: (1) in 'concentration' or percentage contents of the sulphate; and (2) in being much more readily soluble in water; the sulphate, in fact, is soluble in twice its weight of cold water, whereas potash alum requires 18 parts for complete solution.

In addition to the purer forms of the sulphate there are a number of products in the market containing more or less of insoluble matters, representing residues of the original or aluminous mineral not attacked by the sulphuric acid.

The amount of alum or sulphate of alumina added to a pulp is largely in excess of the quantity necessary to precipitate the rosin soap; as a matter of fact, in the case of esparto or straw pulps, for the bleaching of which considerable quantities of bleach have been employed, and which therefore contain a certain amount of basic lime, together with calcium chloride, complete precipitation of the size is effected without the addition of alum. A certain amount is also required to precipitate the starch. The excess of alum appears to be necessary, however, not only to brighten the colour of the paper, but also to render it capable of resisting the action of ink. From experiments made by the authors, it appears that one part of rosin requires 2·9 parts of alum for complete precipitation from its solution in soda. One part of starch requires 0·40 part alum.

Mineral Filling and Loading Agents.—It is usual, except in the case of papers of the very highest quality, to add to the pulp a quantity of some relatively cheap mineral loading material, such as china clay, or for certain qualities of paper, 'pearl-hardening,' or sulphate of lime. The addition of clay in moderate quantity can hardly be looked upon as an adulteration, since it serves to fill up the pores of the paper, thus giving a sheet of closer texture, with a smoother surface and more absorbent of printer's ink, and also enables it to take an improved surface in the subsequent operations of calendering. It also adds to the opacity of the paper—a very important point in book papers. Moreover, it enables the manufacturer to meet the demand for cheap papers with some chance of remuneration to himself. If added largely, it of course tends to weaken the paper.

China clay, or kaolin, is sold in the form of large lumps of a white or yellowish-white colour. It is formed by the gradual disintegration of felspar under the action of air and water, and consists essentially of a silicate of aluminium. Its quality depends upon its whiteness, and its freedom from the coarser micaceous particles. It is usually prepared for admixture with the pulp by making it into a fine cream with water in a vessel provided with stirrers; it is then passed through a fine sieve in order to remove any impurities it may contain, and is then run into the beater. The clay or other filling material is usually run into the beater as soon as the latter is charged with pulp, so that by the time the beating operation is concluded a perfect admixture of pulp and clay is effected.

Sulphate of lime, or 'pearl-hardening,' is usually sufficiently pure to put direct into the engine. It is made by decomposing a solution of calcium chloride with sulphate of soda, and is precipitated as a fine brilliantly white powder consisting of $CaSO_4 + 2H_2O$.

Two distinct forms of precipitated calcium sulphate are met with in commerce, differing from each other by their microscopical features, the one consisting of flat tabular crystals (Fig. 42), the other of fine needles (Fig. 43). Another form, erroneously called 'precipitated pearl-hardening,' is also sold: it consists of the finely ground native mineral, The use of these sulphates is attended by the disadvantage of their solubility in water—which occasions loss on

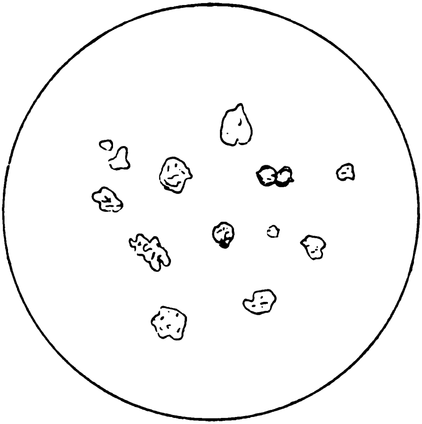


FIG. 41.

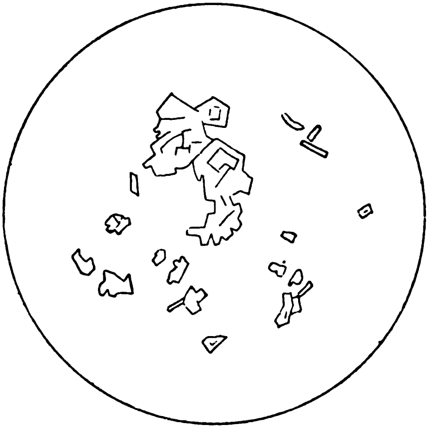


FIG. 42.

the machine. This is, of course, minimised in long runs on the machine, when the 'back water' becomes saturated with the sulphate.

Some of the finer qualities of paper are made without addition of any loading material whatever, though such papers are of course the exception. The proportion of clay or other material that can be retained by a fibre depends to a certain extent upon the nature of the fibre, and upon the

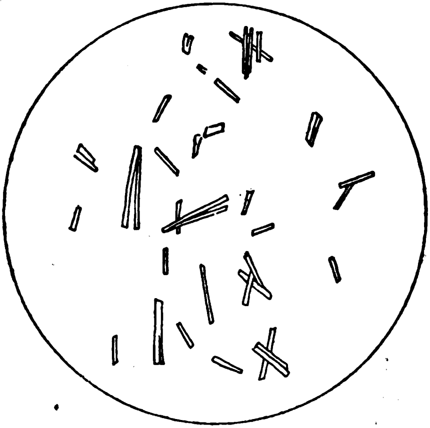


FIG. 43.

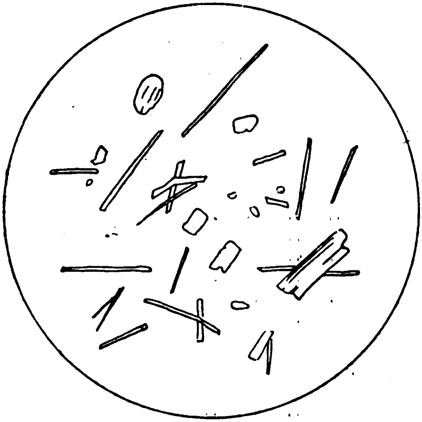


FIG. 44.

degree of fineness to which it is reduced in the beater. The amount added by different makers varies considerably, from 2 or 3 p.ct. to 20, and even in rare cases to 30 p.ct.

Other mineral filling agents having a certain fibrous character have been from time to time introduced, possessing certain advantages over china clay or calcium sulphate. Agalite is a mineral of the nature and chemical properties of asbestos: it consists of nearly pure magnesium silicate. Its structure is more or less fibrous, like that of asbestos, which, as is well known, can be spun and woven and even made into paper, and therefore, when added to a paper, it forms a part of the fabric itself. It is even claimed that it assists in keeping back some of the finer fibres that invariably find their way through the meshes of the wire-cloth, and it is said that 90 p.ct. of the amount added to the engine is found in the paper. In the case of china clay it is well known that only from 40 to 60 p.ct. is often actually 'carried' by the pulp. Figs. 41, 42, 43 and 44 show the appearance of china clay, pearl-hardening and agalite when viewed under the microscope, magnified 200 times. The nature of agalite is such that it assists the paper in taking a high finish. This is probably due to its 'soapy' nature, a feature which is characteristic of asbestos, French chalk, 'soap-stone,' and other magnesium silicates.

The following analysis of china clays may be cited:—

Alumina	39·74	33·44
Iron oxide	0·27	1·04
Calcium	0·36	1·01
Magnesium	0·44	0·16
Silica	46·32	42·72
Water	12·67	20·93

Sp. gr. varying from 2·5 to 2·8.

The following is an analysis of 'agalite':—

Magnesia	32·12	30·70
Iron oxide	0·10	—
Alumina	0·31	—
Silica	62·01	61·90
Water	4·30	—

Sp. gr. varying from 2·6 to 2·8.

When writing papers contain such excessive quantities as 15 or 20 p.ct. of clay, it cannot be to the advantage of the consumer, and should be looked upon as an adulteration.

Analytical Determination of Loading.

It is a matter of some importance to be able to determine rapidly and accurately the amount of mineral matter in a paper. The usual method is to ignite a weighed quantity of the paper in a platinum crucible until the ash so obtained is either white or a very pale grey. From the weight of the ash, the percentage of mineral matter is easily calculated.

In certain cases it may be necessary to take into account both the normal ash of the paper and that due to other added mineral matter. This requires an analytical investigation of the total ash obtained, and a careful interpretation of the results. We can only note here that the processes of treatment add chiefly *lime salts*, which are obtained in the ash mainly in the form of carbonate.

The ignition may be performed in an open platinum dish, and to hasten the complete combustion of the carbonaceous residues the dish should be covered with a piece of platinum foil, bent in the middle to allow free access of air.

A cage of platinum gauze or a closely wound spiral of platinum wire is sometimes substituted for the dish or crucible.

The weighings may be performed upon any balance of sufficient delicacy for the degree of accuracy required. A spiral balance of the form devised by Joly, and fully described in the First Edition of this book, is a convenient instrument for rapid work.

In brown and coloured papers various *coloured mineral loading agents* are used; thus the ochres, which are chiefly oxides of iron, chrome yellows, chiefly chromate of lead.

Ultramarine in heavy blue papers is used in sufficient quantity to have a certain 'filling' effect.

These substances or their products of decomposition are obtained in the ash. If clays or other loading agents are also present, the proportion of pigment-loading may be approximately estimated by separating its characteristic constituent by suitable analytical treatment of the ash.

If the paper contains calcium sulphate, the ash obtained may consist partly of calcium sulphide, due to reducing action of the carbon found on ignition, and the amount will therefore not represent the true amount added. The ash should be moistened with a few drops of sulphuric acid, and again ignited, in order to reconvert it into calcium sulphate. It should also be borne in mind that the sulphate of lime as present in the paper is combined with two atoms of water $CaSO_4+2H_2O$, and therefore that every part of calcium sulphate obtained represents 1·26 parts of 'pearl-hardening' actually in the paper.

Colouring.—The colouring of paper in the paper-mill is effected by the addition of pigments or solutions of dyestuffs to the pulp in the beater. Colouring with pigments is, of course, a purely mechanical operation. At the same time it must be remembered that many of the paper-makers' pigments are reactive chemical compounds, and when acted upon by substances present in the beater, e.g. rosin-size and alum, may be destroyed or modified, with attendant loss of colour or alteration of shade. Attention must be paid, therefore, to the chemical composition of pigments, in order that their full colouring power may be realised and permanently retained in the paper. The soluble dyes are for the most part artificial products of well-defined chemical constitution. An intelligent application of these products by the paper-maker presupposes an intimate knowledge of the general principles of the dyer's art. We may note, however, at this point, that the makers of coloured papers are comparatively few; whereas, on the other hand, there are few papers made which do not receive some addition of colouring matter. Thus all bleached pulps retain a residual yellow tint more or less pronounced, and for white papers the yellow requires to be 'neutralised' or 'corrected' by the addition of blue and red, producing a 'neutral' or dyed white In effect these dyed whites are greys, but the balance or neutralisation of colour produces an illusive impression of whiteness. In view of their more general importance we shall deal first with colouring matters and methods used in producing these dyed whites.

1. The following are the more important colouring matters:—

BLUES.—*Ultramarines* of various shades, tending on the one side to red, on the other to green tones ot blue. The modern ultramarines are artificial products consisting essentially of silica, alumina, soda and sulphur, and are prepared by fusing together mixtures of raw materials furnishing these components. The coloured body itself may be regarded as a sodio-aluminic silicate, united either with a polysulphide of sodium or with a polysulphide and polythionate. These relationships are expressed by the following formula:—

$$2Al_2O_3 : 3SiO_2 : Al_2O_3 : 4SiO_2 : Na_2S_2O_3 : 3Na_2S.$$

The compound is attacked by the mineral acids, hydrogen sulphide being liberated; it is also rapidly attacked by chlorine and oxides of chlorine. The decomposition is synonymous with destruction of colour.

Smalts.—This is a pure blue pigment obtained by reducing a cobalt-glass to the finest state of division. The glass is essentially a potassio-cobaltous silicate,

$$K_2O \cdot CoO \cdot 6SiO_2,$$

with varying proportions of alumina and iron oxide as incidental impurities. The deep-coloured varieties contain 6–7 p.ct. CoO; 70–72 p.ct. SiO_2; 17–21 K_2O (with Na_2O). This pigment is extremely permanent and resistant to chemical action. On account of its high price it is used only in papers of the highest quality.

Soluble Dye-Stuffs.—The blues and violets used in tinting for whites are chiefly 'aniline' derivatives. The '*soluble blues*' are the sulphonic acids of phenylated rosanilines. The '*methyl violets*' are methylated rosanilines. The induline class of blues are greyish blues of various tones, obtained as by-products in the manufacture of rosaniline. They are oxidation products of aniline. This group includes the nigrosines, Blackley blue, etc.

Methylene Blue is a useful fast blue, of pure tone, and is obtained from dimethyl-paraphenylene-diamine by the action of sulphides and subsequent oxidation. It contains sulphur as an essential component.

REDS, of the pigment or lake class, are seldom used in tinting for whites.

Soluble Dye-Stuffs.—Of these, one of the most important is the colouring matter of the cochineal insect. From the raw product a dye liquor may be prepared, either by exhaustion with boiling water or by long steeping of the material with strong aqueous ammonia in a closed vessel. The latter is the more convenient method. After steeping, the mass is thrown on to a conical flannel bag, which is then suspended in a vessel of water. By diffusion, followed by squeezing and washing, the exhaustion of the colour is completed. 5 lbs. of material treated in this way will make 10 gallons of 'cochineal liquor' of ordinary working strength.

Of the coal-tar dyes, the paper-maker uses (1) of the rosaniline group, the various magentas; (2) the safranines which are poly-aniline derivations; (3) azo-dyes, derived from benzidine, especially benzo-purpurine; and (4) the eosines, which differ essentially from the three preceding groups in containing no nitrogen: they are derivatives of the coal-tar phenol resorcin, and not of nitrogenous bases.

Applications.—The use of the above colouring matters in white papers involves, for obvious reasons, very small proportions. Of the blue pigments an average proportion is 0·1 p.ct. of the weight of the 'furnish'; of cochineal 0·01–0·02 p.ct., calculated as original cochineal per 100 lbs. furnish. The coal-tar dyes, having greater tinctorial power, are used in still less proportion. There are no general rules which can be laid down as to the stage in the beating process when the colour should be added. Where, however, the colouring matter is not affected by the rosin size, it is better to add it while the contents of the beater are alkaline from its addition. The soluble dyes should not be added in the form of the ordinary stock solution, which may contain from 2 to 5 p.ct. of the dissolved dye stuff. This should be diluted considerably before adding to the beater, and well distributed in adding it.

2. *Coloured papers*, as distinguished from whites—which are dyed whites—and self-coloured papers are produced with larger proportions of colouring matters. To those used in tinting for whites we have to add other blues, and reds, and also those giving yellows and browns, and also greens. The following are the more important:—

Prussian blues of various grades. These are the ferroso-ferric ferrocyanides formed by decomposing a mixture of ferrous and ferric salt in solution, with a soluble ferrocyanide. These blues are sold in paste form, under various trade names. They are recognised by being at once decolorised by the caustic alkalis, the basic iron oxide being left as a brown residue.

These blues are often formed by bringing together the above-mentioned salts in the beater, i.e. a mixture of ferrous and ferric sulphates (copperas and 'red iron liquor') added first and followed by the equivalent quantity of potassium ferrocyanide (yellow prussiate). Dyeing with prussian blue in this way is carried out after the sizing operations are complete. It may be noted here that all paper 'furnishes' contain iron compounds as an impurity, in greater or less degree, and in some cases this is taken advantage of for conversion into the blue ferrocyanides by addition of the potassium salts to the beater in correspondingly small proportion.

Logwood.—The aqueous decoction, or the concentrated extracts sold in the trade, are used in producing the darker shades of blue, usually in admixture with Prussian blue; also for a larger number of heavy mixed shades and for blacks.

Alizarin (madder).—This most important red dye is not used directly in colouring papers. It occurs in the form of pigments or insoluble lakes, which are compounds of the colouring matter with alumina, etc.

Alizarin printed cottons and 'Turkey red' rags may be beaten after the alkali treatment to a coloured pulp.

Iron oxide pigments cover a wide range of gradations of colour from the *reds* (rouge) to browns (the brown ochres), and from these to the yellows of the 'yellow ochres.'

Yellows.—Of the pigment class the most important is the brilliant chromate of lead. This is usually formed in the beater by the interaction of lead acetate and the alkaline bichromates.

Of coal-tar dyes the more important yellows are Auramine, a basic dye-stuff, a derivation of dimethyl-aniline; *naphthol* yellow, which is the alkali salt of di-nitro-naphthalene; *primuline*, a sulphur-containing derivative of toludine; and a large number of azo and amido-azo derivatives, such as the tropaeolins, chrysoidines.

Greens.—The mineral green pigments are but little used by the paper-maker. Mixtures of blue and yellow pigments, e.g. Prussian blue and lead chromate, are however employed. The more important coal-tar dyes are malachite green, a derivative of rosaniline, and 'acid' greens, which are the sulphonic acids of the group of the 'malachite' or benzaldehyde greens.

Browns.—In dyed browns the paper-maker uses a number of pigments of the iron oxide group.

Of soluble dye-stuffs an important group is furnished by the 'natural' astringents, or tannin derivatives, e.g. catechu and gambir. The catechu liquor is prepared by boiling the finely powdered raw material for 2–3 hours with 3–5 times its weight of water. When cold, a solution of sulphate of copper, calculated to 6 p.ct. of the weight of the catechu, is added. In using these tannin colouring matters, bichromate of soda is used to develop or intensify the brown, iron salts for deepening or blackening the shades.

A medium brown is obtained with 4 p.ct. catechu on the furnish, 'developed' with one-sixth its weight of the bichromate. Of coal tar dyes there are a large number of browns. The well-known Bismarck browns are salts of tri-amido-azobenzene.

Applications.—The dyeing of paper pulps in the engine is an art which can only be said to be grasped when the whole of the factors involved are intelligently followed. To do this it is necessary to take into account all that has been advanced in the earlier chapters as to the constitution of the celluloses, their general inertness, accompanied by graduations in chemical reactivity such as obviously affect their relationships to colouring matters, the combination with which is undoubtedly a chemical phenomenon. Therefore also the constitution of the colouring matters themselves must be taken into account. Lastly, owing to the inertness of the celluloses and more especially those of the cotton group, the cotton dyer is limited to comparatively few dyes or groups of dyes which combine directly with the fibre: in the majority of his processes he requires the assistance of intermediary substances known as *mordants*—compounds which combine directly with the fibre-substance *and* the colouring matter, and which therefore in combination with the former enable it to take up and fix the colour in the insoluble condition.

Owing to the development of the industry in coal-tar colours, and the enterprise of manufacturers, the paper-maker is certainly saved much trouble by being supplied not only with a practically infinite range of colours, but with working specifications of methods of using them, including particulars as to the mordants required. In view of this extensive specialisation, we make no attempt to treat the subject in detail. The student must be referred to such special treatises as the following:—

(1) On the general principles of dyeing: 'The Dyeing of Textile Fabrics,' by J. J. Hummel (London, Cassell & Co.).

(2) On the constitution of the colouring matters: 'The

Chemistry of the Coal Tar Colours,' by Benedikt and Knecht (London, G. Bell & Sons); and

(3) For working formulæ for the colouring of pulp in the engine, those contained in J. Dunbar's 'The Practical Paper-Maker' (London, 1887, Spon) are useful and typical of a wide range of effects.

The paper colourist may either work on purely empirical lines, i.e. by means of recipes and specifications supplied to him; or he may by his own investigations devise endless combinations to produce special effects, or produce the usual effects by specially economical means. In either case it may be pointed out that since uniformity is of the utmost importance, all conditions of preparation and treatment must be kept rigidly uniform.

In matching colours, allowance must be made for the condition of the stuff in the beater, and alterations of shade which take place during the process of making into paper—(1) by incidental variations in the composition of the back-water in the machine; and (2) by the action of the heat of the drying cylinder. The usual practice of matching is to make up a sheet of paper in a hand-mould from the stuff in the beaters, which is then pressed and dried on a hot cylinder or steam pipe. The examination of the colour by comparison with the sample requires care and attention. A good 'white' light must be chosen, preferably daylight in a north aspect. Matching at night requires that the artificial light shall be of exceptional purity.

During the time that the loading, sizing and colouring processes have been going on, the pulp has been continually acted upon by the roll, and if these operations have extended over a considerable time, it is probably in a proper condition for making into paper. The amount of 'beating' depends, as has been stated before, upon the nature of the fibre, and also to some extent on the nature of the paper for which it is intended. The 'beaterman' examines the pulp from time to time by taking a portion from the engine and placing it in a hand-bowl containing water: from its appearance when so diluted he is able to judge of the time during which it may be necessary to continue the disintegration. As soon as this is completed, the pulp is ready to be let down to the stuff-chests, usually placed at a lower level than the beaters, so that the pulp can flow into them by gravity. For this purpose the valve at the bottom of the engine is opened: to remove the last portion of pulp it is necessary to rinse out the engine with water.

CHAPTER IX.

PAPER MACHINES; HAND-MADE PAPER.

THE pulp as it comes from the beaters is now ready to be made into paper. We will first consider briefly the manufacture of hand-made paper.

It is made on a mould of wire-cloth, with a movable frame of wood, called the 'deckle,' fitting on to the outside of the mould, and extending slightly above its surface.

The wire-cloth is generally supported by a much coarser wire-cloth, or by pieces of thick wire, and these again by wedge-shaped pieces of wood, the thin end being next to the wire.

To form a sheet of paper the workman dips the mould with the 'deckle' in position, into a vat containing the prepared pulp diluted with water, lifting up just so much as will make a sheet of the necessary thickness. As soon as the mould is removed from the vat, the water begins to drain through the wire-cloth, and to leave the fibres on the surface in the form of a coherent sheet of paper. The felting or intertwining is assisted by lateral motion in every direction given to the frame by the workman. The movable deckle is then removed, and the mould, with the sheet of paper, given to another workman, called the 'coucher,' who turns it over and presses it against the felt, by this means transferring the sheet from the wire to the felt. In the meantime the 'vat-man' is engaged in the formation of another sheet with second mould.

A number of the sheets thus formed are piled together, alternately with pieces of felt, and when a sufficient number have been obtained, the whole is subjected to strong pressure, to expel the water. The felts are then removed, and the sheets again pressed.

They are then sized, if required, by dipping them into a solution of gelatine: again slightly pressed, and hung up on lines or poles to dry. Such paper is called loft-dried.

When dry the sheets of paper are calendered. (See Chapter X.), plate-glazed or otherwise finished.

The making of paper by hand involves considerable dexterity on the part of the workman; on account of the expensive labour necessary, in comparison with paper-machines, it is comparatively little practised in the present day; certain kinds of paper, however, such as bank-notes, various drawing papers, and printing papers intended for the production of very elaborate editions are made in this way.

Any pattern or name required on the paper is obtained by means of a raised pattern on the wire-cloth mould: consequently, less pulp lodges there, and the paper is proportionally thinner, thus showing the exact counterpart of the pattern. Such devices are known as 'water-marks.' (See also p. 222.)

The Paper Machine.—The paper machine of the present day, with all its ingenious improvements, differs but little in principle from that originally constructed by Fourdrinier. It consists essentially of an endless mould of wire-cloth, on to which the prepared pulp flows, and on which a continuous sheet of paper is formed. The sheet of paper then passes through a series of rollers and over a number of heated cylinders, where it is completely dried.

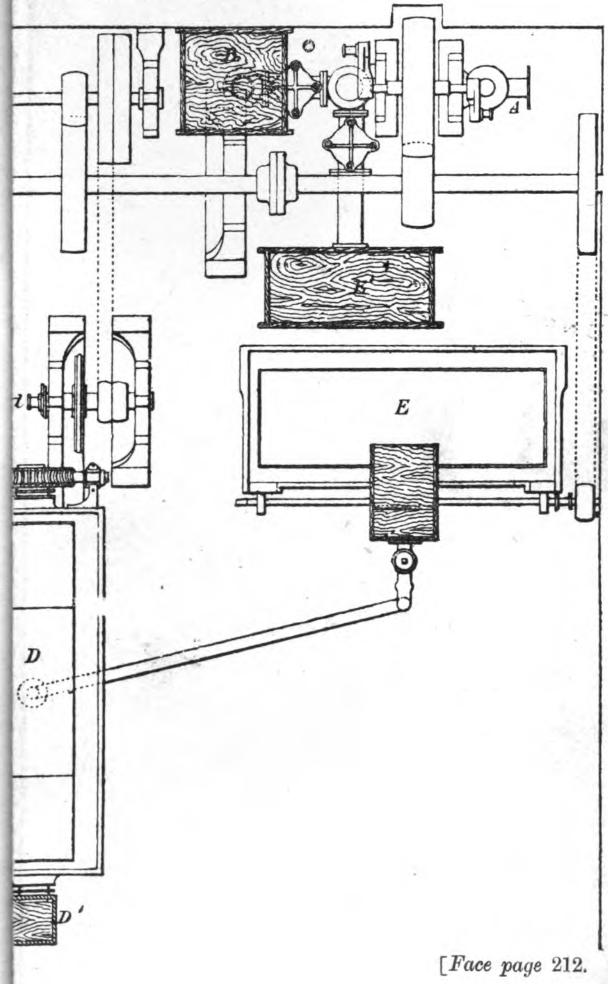
A modern Fourdrinier paper machine is shown in side elevation and plan in Plates I. and II.

The pulp, after leaving the beaters, passes into a large vessel called the stuff-chest, of which there are one or more to each machine. In emptying the beater water is run in to thoroughly rinse out the remaining pulp, the washings also going into the stuff-chests. These may be made either of wood or iron, and should be provided with arms fixed on a vertical shaft, made to revolve by suitable gearing. The arms are for the purpose of keeping the pulp thoroughly mixed, and should only work at a moderate speed, otherwise they are liable to cause the fibres to form into small knots or lumps. The pulp is drawn from the stuff-chests by means of the pump A, and is discharged into a regulating-box (not shown). The object of this box is to keep a regular and constant supply of pulp on the machine. It consists of a cylindrical vessel, having two overflow-pipes near the top, and a discharge-pipe near the bottom. The pulp is pumped in through a ball-valve in the bottom, in larger quantity than is actually needed, the excess flowing away back into the stuff-chests, through the two overflow-pipes. By this means, the box is always kept full, and therefore the stream of pulp issuing out of the bottom pipe is always under the same pressure. It flows from this pipe, the quantity being regulated by means of a cock, according to the thickness of paper required, directly on to the sand-tables. These may be of various sizes and shapes, but should be so large that the pulp takes some little time to travel over them. They consist of long shallow troughs, generally of a sinuous form. The bottoms are sometimes covered with woollen felt, or with thin strips of wood placed across the direction of the flow of the pulp, and at a slight angle. These serve to retain any particles, such as sand and dirt, that may have escaped removal in the previous treatment of the pulp, and that are heavy enough to have sunk down during the passage of the pulp along the sand-tables. In some mills, where great care is exercised, the pulp is caused to flow over sand-tables 200 yards in length. As the pulp, when it leaves the stuff-chests, does not contain sufficient water for the purpose of making paper, it is mixed, where it enters the sand-tables, with a quantity of water from the 'save-all' (see p. 221), flowing from the box B placed at a higher level.

In some mills, instead of being pumped into the regulating-box, the pulp flows into a small vessel below the stuff-chest,


M
r
u
h
k

PLATE II.



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212.

and is lifted on to the sand-tables by means of buckets fastened on the circumference of a wheel.

The pulp, after leaving the sand-tables, passes on to the strainers. These consist of strong brass or bronze plates, having a large number of very fine V-shaped slits cut in them, the narrowest end being on the outside.

Strainers.—The strainers are for the purpose of removing from the pulp all lumps formed by the intertwining of the fibres, and all pieces of unboiled fibre, which, if allowed to pass on, would show in the paper as inequalities in the surface, or as dark specks. The slits are made narrow at the top, and gradually increasing in width, so as to prevent them from getting choked up. These slits allow only the individual fibres to pass through, and their width varies according to the quality of the paper. They are from 2 to 3 inches long, and they vary in width from ·007 to ·05 inch. They are put at distances of about ¼ inch apart. Several plates, each containing about 500 slits, are bolted together and form a strainer. The whole strainer receives a violent shaking motion, to assist the passage of the fibres through the slits. In the machine represented, two of these strainers are shown at C. The shaking motion is produced by the ratchet-wheel or cams *a* acting on the hammer *b*. An improved form, called the 'revolving strainer,' has of late years been introduced. The pulp generally passes first through one of these, and then through the ordinary or 'flat' strainers, as they are called. A revolving strainer is shown at D. It consists of a rectangular box, the sides of which are formed of plates perforated with slits. Inside this box, a slight vacuum is formed by means of an indiarubber bellows worked by a crank on the shaft *d*. The vacuum is intended to serve the purpose of the shake in the ordinary form. The box revolves slowly inside a vat containing the pulp, and the strained pulp flows into the box D^1, and thence on to the flat strainers.

Various patents have been taken out from time to time for flat strainers worked by means of a vacuum underneath the plates caused by the motion of discs of indiarubber or thin metal. Fig. 45 shows in plan a set of strainers, as manufactured by Messrs. G. & W. Bertram, similar to those in Plate II., but illustrated somewhat more in detail.

The pulp first passes through the flat strainer B, and from thence to the two revolving strainers A. From these it flows along the shoots placed at the side on to the paper machine at E.

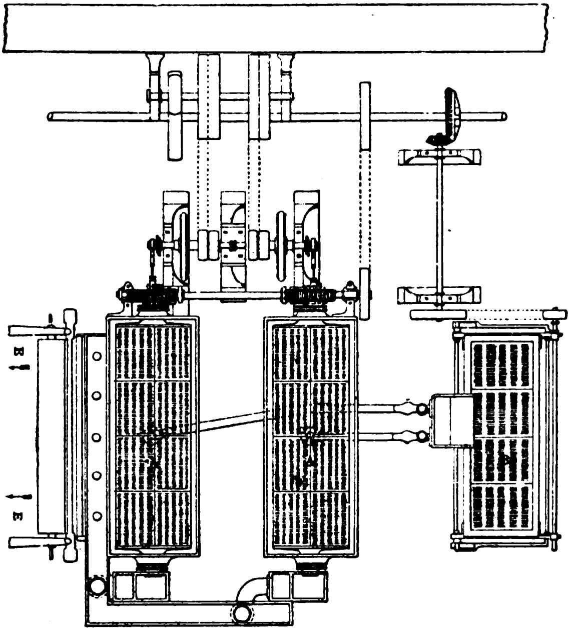

FIG. 45.

Fig. 46 gives a view of a patent flat vacuum strainer made by the same firm, which may also be used for cleaning straw or esparto previous to its passage over a *presse-pâte*. The pulp flows on to the strainer at *a*, and passes away by the cast-iron pipes *f*. The valve *g* is for running off waste pulp. The plates are placed at a slope of about 1 in. in their length; those nearest the supply of pulp are provided with coarser slits, as the impetus carries the knots forward. The vacuum pumps are worked by the rods *d* from the shaft *e*. By means of the tube *c* water can be directed on to the plates, whereby the coarser particles of fibre are carried forward, and the slits are kept clean. The plates can be removed in a few minutes.

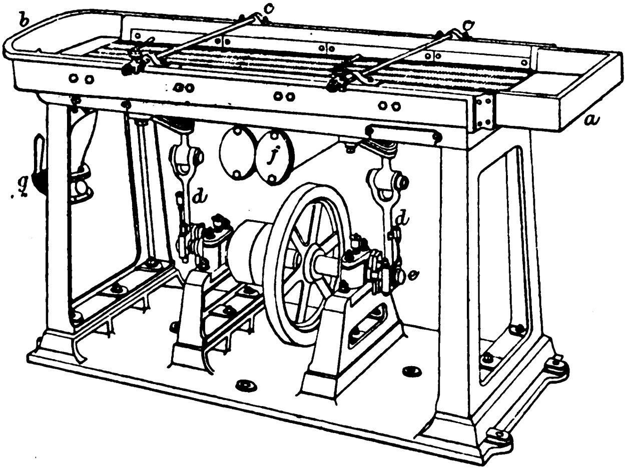

FIG. 46.

Figs. 47 and 48 show in side and end elevation, Messrs. Masson, Scott & Bertram's patent self-cleaning strainer. The novelty consists in an arrangement by means of which the upper surfaces of the plates are continually freed from those portions of the pulp which cannot pass through the slits.

The scrapers *d* are made of vulcanised indiarubber, and are continually carried forward by an endless chain; the knots, &c., collect in a heap at the end of the strainer. The pulp flows on at *a*, and passes away through the pipe *b*. The pumps are driven from the shaft *e*.

Messrs. C. H. & F. L. Roeckner's patent strainer (No. 7932, 1885) consists of a series of cylindrical tubes, open at one end and perforated with slits. They are placed in a vat into which the pulp flows. Inside the cylinders are placed two, three, or more plates fixed to the shafts on which the cylinders are supported, and extending to the circumference. These plates form a kind of fan, which, together with the cylinders, are caused to oscillate by means of a rod and cranks. This oscillating motion serves to draw the fibres through the slits, and at the same time to keep the outsides of the cylinders clean. The cylinders are easily removable.

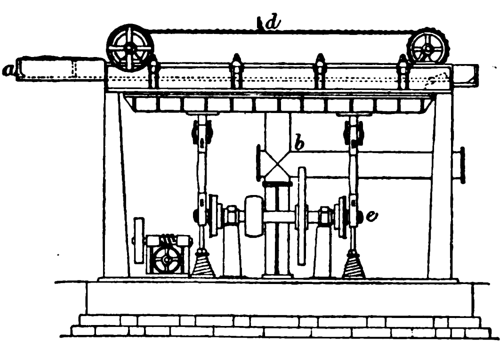

FIG. 47.

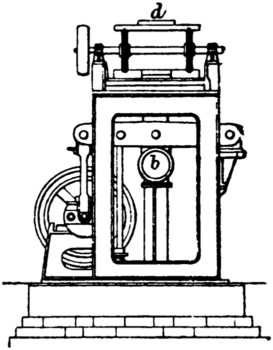

FIG. 48.

After a time, the slits in the plates get too large, owing to the plate having been worn away by the constant friction of the fibres, and as they are very expensive, various attempts have been made to invent plans for partially closing them again. Hammering will effect this, but is liable to break the plates. Annandale of Beltonford has introduced a method of closing the plates, by means of heavy pressure acting on small steel rollers moving on each side of the slit, in which is placed a small sheet of metal the exact thickness of the width desired.

Another method of closing the plates consists in filling them up by means of electrically deposited copper or other metal. They can then be recut in the usual way.

In the case of revolving strainers, all that cannot pass through the slits falls to the bottom of the vat, in connection with which it is customary to have an auxiliary strainer, or 'patent knotter,' as it is called, shown at E. All fibre that passes through this one, which is of the ordinary flat kind with shaking motion, goes into a box near E′, called the 'low box' for 'save-all' water (see p. 221).

The pulp, after passing through the strainers, should be perfectly free from knots and impurities, and in a fit condition for making paper. In the machine shown, it passes from the last strainer directly on to the wire, its flow being regulated by a movable gate *e*. In some cases, however, it first flows into a small vat, in the centre of which revolves a rod carrying paddles, with the object of keeping the pulp well stirred up. It is carried right on to the wire by means of the apron, a piece of canvas, oil-cloth, or sheet rubber, one end of which is fastened to the breast-board *e′*, the other end resting on, and covering the wire to the extent of about 15 inches. The edges of the apron are rolled up to prevent the pulp from overflowing. After leaving the apron, it passes under a gate, or 'slicer,' as it is sometimes called, made of two pieces of brass, overlapping each other in the centre, and bolted together. It is made thus to enable it to be lengthened or shortened according to the width of the paper; its height from the wire-cloth can be altered by means of screws, and should be equal at all points, in order to ensure a uniformly thick sheet of paper. The ends of the two pieces forming the slicer are fastened to the frame *f* or 'deckle,' as it is called, and this again is carried by two or more rods stretching right across the wire, and fastened by small upright supports on both sides to the frame *g*. The deckle-frame also carries the grooved pulleys *h*, along which the deckle-straps *i*, endless square bands of indiarubber, move.

The object of the deckle-straps is to regulate the width

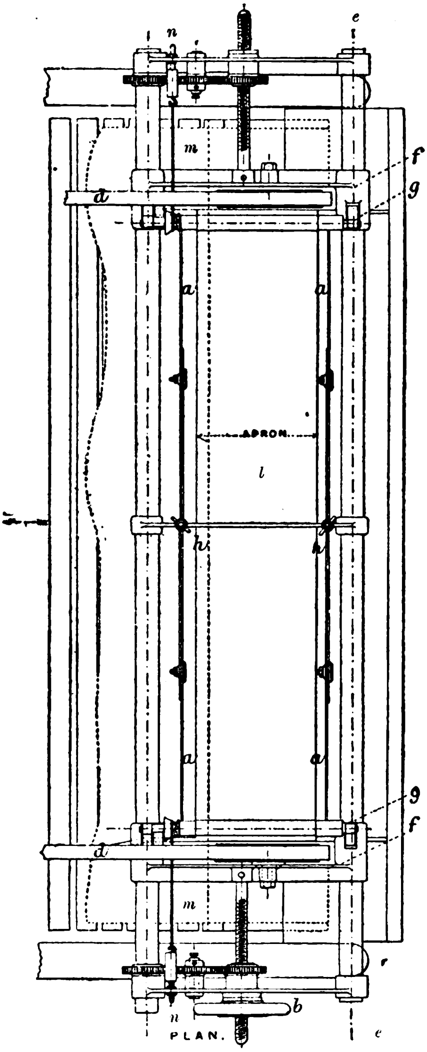

FIG. 49.

of the paper; they form, together with the wire-cloth, a kind of mould into which the pulp flows, thus corresponding to the mould used in producing hand-made paper. The width of the paper can be altered by shifting the position of the frame *f*, and also the deckle-straps, which are carried on it as described, the pulleys *h* being so arranged that they slide along the rods on which they revolve. In order to alter the width of the paper it is necessary to stop the flow of pulp on to the wire, and it not only consumes a considerable amount of time, but generally necessitates a partial cleaning up of the machine. Various attempts have, therefore, been made to devise an arrangement whereby the change can be effected while the paper is being made. Several contrivances have lately been introduced, all similar to the one shown in Figs. 49 and 50.

In it the frame *f* carrying the deckle-strap is made to slide along the rods *e* by means of the small wheel *b*, and by a similar arrangement on the opposite side and geared with it. The movable apron *l*, Fig. 49, is wound round the spindle *g*, and is kept taut by the cords *m* connected with the springs *n*. As the deckles approach each other, the excess of apron is wound up, when they are separated it unwinds again. The flow of pulp is regulated by two slices *a a*, which are kept in position by the screws *h*. The whole arrangement is securely bolted to the frame of the machine; *c* (Fig. 50) represents the breast-roll, and corresponds to **F**, Plates I. and II.

The thickness of the paper is regulated by altering the supply of pulp to the wire-cloth, and by the speed at which the machine is working. This speed may vary from about 60 feet to as high as 500 feet per minute.

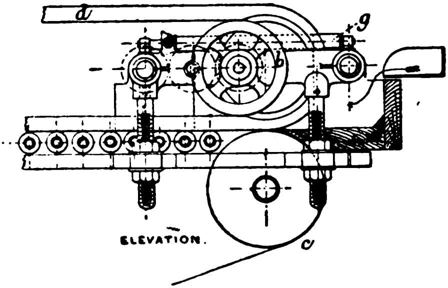

FIG. 50.

The 'wire' is an endless cloth made of very fine wire, the fineness depending much on the quality of the paper required. The mesh varies from 60 to 70 and even more threads to the inch. It is not woven endless, but is joined by very careful sewing with wire. Its width varies considerably, some being made as wide as 126 inches; the length is generally 35–40 ft. It is carried by the breast-roll F, the lower couch-roll G, and the small rolls *f*; and by a large number of small rolls f''. The latter and the breast-roll are supported by the frame *g*, while the small rolls f' are supported by brackets attached to it. The course of the wire is indicated by the arrows. The frame *g* works on two pivots *g*′, and receives a shaking motion from side to side from the rod *j*, in connection with a crank worked by two conical drums H. The supports *g*″ are also pivoted at their lower ends to allow for the shaking motion. This shaking motion is given for the purpose of weaving or intertwining the fibres. One or more of the rolls *f*′ can be moved up or down on the support which carries it, for the purpose of stretching the wire. There is usually a large number of the small rolls *f*″, as it has been found by experience that, probably owing to capillary attraction, they cause the water to leave the pulp. Though a large quantity of water thus passes through the wire-cloth, it is necessary to assist it by artificial means. This is done by means of the suction-boxes I connected by pipes with the vacuum-pumps I′.

This part of the machine, which is called the "wet-end," is placed at a slight slope of about 1 in. in its entire length, the lowest end being nearest the strainers.

Underneath the wire-cloth is placed a box called the 'save-all' K, connected with the box E′. The water that passes through the wire-cloth contains a considerable quantity of very fine fibres, together with size, alum, clay and colouring materials, that have passed through the wire, and which would be lost but for the arrangement now universally adopted. It flows into the box E′, and is pumped, together with the pulp that has passed through the knotter E (see p. 217), into the high box B, whence the mixed stuff flows on the sand-tables, to be again used to dilute fresh pulp from the stuff-chests. The following numbers will give some idea of the nature and amount of fibres, &c., which pass through. The paper was made from esparto and straw, sized with rosin and starch. It contained 12 p.ct. of clay.

	Grains per Gallon of Waste Water.
Fibre	34·37
Clay	37·10
Starch	1·40

It is almost impossible to utilise the whole of the back-water passing through the wire-cloth in the way described. In some mills a portion of this water is made to pass through a 'pulp-saver,' such as is shown in Fig. 51 and 52. It consists of a conical drum A, the circumference of which is covered with wire-cloth, and it is caused to revolve slowly by suitable gearing. The water enters by the pipe B, and passes through the meshes ef the wire-cloth, the pulp gradually finding its way to the wider end, where it is discharged into the box C. It can then be returned to the beaters.

The pulp-saver can also be used for recovering the fibre from other waste water, such as the wash water from the washing and beating-engines; or it can be used for freeing bleached pulp from water in cases where drainage or hydraulic pressure is not resorted to.

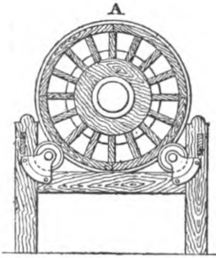

Fig. 51.

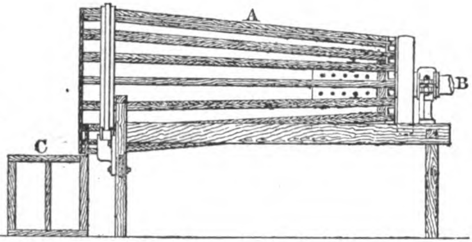

Fig. 52.

If any pattern or name is required on the paper, it is produced by means of a light skeleton roll, call a 'dandy-roll,' covered with raised wires in the form of the desired pattern, placed between the suction-boxes, and pressing lightly on the still moist paper. The paper is thinned where the wire pattern presses, and thus a mark (water-mark) is produced. The other side of the paper has a mark corresponding to the wire-cloth; by using a dandy-roll covered with wire-cloth, the two sides can be obtained alike, such paper going by the name of 'wove.'

Paper in which a series of parallel lines are produced is called a 'laid' paper.

Some water-marks are produced by means of a dandy-roll in which the pattern is formed by depressions in the surface. The paper is thus *thicker* where the pattern is formed than in the ground-work. De la Rue (Patent No. 8348, 1884) has patented the use of dandy-rolls so formed as to produce upon the paper the effects both of thickening and thinning.

Imitation water-marks can be produced on the finished paper by subjecting it to pressure in contact with plates on which the design has been produced in relief. In this way very beautiful results can be obtained. (See Patent No. 13,455, 1884.)

It sometimes happens that the wire-cloth slips slightly to one side. This can be obviated by the machine-man shifting, by means of screws, one of the rolls provided for the purpose with a movable journal, until its axis is at a slight angle to that of the other rolls. An automatic apparatus has been invented for this purpose. Two brass plates are fixed, one on each side of the wire-cloth, to a long rod, connected by suitable machinery with the screws working the movable journal, so that, as the wire presses against one or the other of these plates, the roll is shifted so as to correct this.

The paper, which, even after passing the suction-boxes, is still very wet, passes with the wire-cloth between the couch-rolls G G′. These are hollow copper or brass cylinders, covered with a tightly-fitting endless jacket of felt. They may also be made of wood (sycamore or mahogany) or of iron or iron and brass combined. The pressure of the upper couch-roll upon the lower can be regulated by means of screws or levers. They serve to press out water from the paper, and to detach the paper from the wire-cloth. By dexterous manipulation on the part of the machine-men, the paper is transferred to the endless felt, travelling over the rolls *k* in the direction of the arrows. It is known as the 'wet felt,' from the condition of the paper at this stage. In its passage along this felt, the paper passes between two iron rolls K, called the first press-rolls, with the object of having the water squeezed or pressed out of it. These rolls are sometimes covered with a thin brass case, and the top one is provided with an arrangement called the 'doctor,' in order to keep it clean, and free from pieces of paper that may have stuck to it. The lower press roll is sometimes covered with an indiarubber jacket. The 'doctor' is a kind of a knife placed along the whole length of the roll and pressing against it at every point. The pressure on the rolls can be regulated by means of levers, or, as in the illustration, by the screw *k'*. It will be readily seen that the under side of the paper that has been next to the felt will, in its still moist condition, have taken to some extent an impression from the felt, while the upper side will have been made comparatively smooth by the pressure against the top roll of the 1st press. In order to make both sides of the paper as nearly as possible alike, it is passed through another set of rolls L, called the 2nd press. This time it is reversed, and enters at the back of the rolls; thus the other side of the paper is next the metal, being taken through by the felt (called the '2nd press felt') travelling on the small rolls *l*, the paper, after leaving the wet felt, and before being taken on to the 2nd press felt, travels over the rolls *l'*. The 2nd press felt is necessary, because the paper is too tender to withstand, unsupported, the pressure of the rolls.

The paper, after passing the 2nd press rolls, travels over the drying-cylinders M, the number of which varies somewhat. In the machine shown, there are in all eight cylinders. Sometimes as many as twelve are employed. Between the 2nd press rolls and the cylinders, a passage S allows easy access to the other side of the machine. The paper generally passes alone over the first two, which are only slightly heated; afterwards it is led over the others by means of felts, as shown. The arrangements shown at R are for the purpose of stretching the felts. The cylinders are heated by means of steam, and are generally divided into two sets, between which is a pair of chilled-iron, highly-polished rolls N, called 'smoothers,' the function of which is sufficiently explained by their name. They are also heated by means of steam. The cylinders are usually made of slightly decreasing diameter, in order to allow for the shrinking of the paper on drying. Messrs. G. and W. Bertram introduce into some of their machines one or two small drying cylinders, over which the 2nd press felt travels, the object being to drive off some of the moisture absorbed from the paper. This contrivance is said to give excellent results, and to ensure a considerable saving in felts. The arrangement is shown in Fig. 53. It is especially useful in machines running at a high speed, or in those having limited drying power. After leaving the cylinders, the paper should be quite dry; it is then led through the calenders, of which there are in some machines as many as three sets, though only one is shown. These are similar to the smoothing-rolls, just described. Pressure is applied by the screws O′, or by levers and weights. The friction of the hot calenders on the dry paper develops a large quantity of electricity, which occasionally discharges itself in bright sparks.

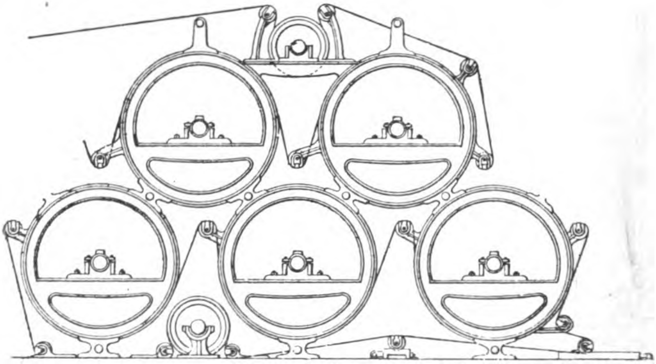

FIG. 53.

It is the practice in some mills to cool the paper before passing it through the calenders. This is effected by passing it over a copper cylinder, through which a stream of cold water runs.

The degree of smoothness or 'finish' that can be given to the paper by the calenders, depends to a large extent upon the degree of moisture which it contains. As it leaves the last cylinder it is perfectly dry, that is to say, it contains only that amount of water which cellulose, from whatever source, always carries. This amount varies slightly with the nature of the cellulose, and with the plant from which it has been isolated, and also with the state of the atmosphere, it being greater on damp days. It would be impossible so to regulate the drying action of the cylinders that the requisite amount of water should always be left in the paper; it is therefore better to dry it as thoroughly as possible, and then to add the water, by artificial means, just before it passes through the calenders. This method, moreover, has the advantage of damping only the surface of the paper.

Fig. 54 shows a damping arrangement as manufactured by Messrs. James Bertram and Son. The paper on leaving the last drying-cylinder passes on to two copper cylinders *c*, filled with cold water. Steam passes through the pipe *a*, and issues through a number of fine holes in a pipe running at right angles to the direction in which the paper is travelling, and near to it. The steam condenses on the paper and on the surface of the cylinders, from which the paper absorbs it. The supply can be regulated by the cocks shown in the drawing. The troughs *d* carry off any excess of condensed water.

Amongst other methods proposed is one by Annandale; it consists in breaking up jets of water into a very fine spray by means of a blast of air.

The finished paper, after passing through the calenders, is wound on the reels P. The gearing by which the whole machine is driven is shown in Plate II.

It sometimes happens that, owing to the increased tension due to the contraction of the paper in drying, the paper breaks. It is therefore necessary to alter the speed of some of the cylinders to compensate for this. A rough expedient which is largely adopted, consists in attaching, by means of a mixture of rosin and tallow, a piece of felt to one or other of the pulleys (Plate II.), and thus altering its speed.

Tub-sizing.—The foregoing description is of a machine for the manufacture of engine-sized papers; some slight modifications are necessary in the case of papers that are tub-sized on the machine. In making the cheaper qualities of tub-sized papers, the paper, after being partially dried over a few cylinders, is passed through a vessel containing a solution of gelatine (see p. 228) It then goes between a pair of rollers, which press out the excess of size, and then again over drying cylinders. The vessel or trough containing the size is filled to overflowing from a tank placed at a higher level; the overflow passes into a lower vessel, from which it is pumped up to the top tank. The size is kept warm by means of a coil through which steam passes placed

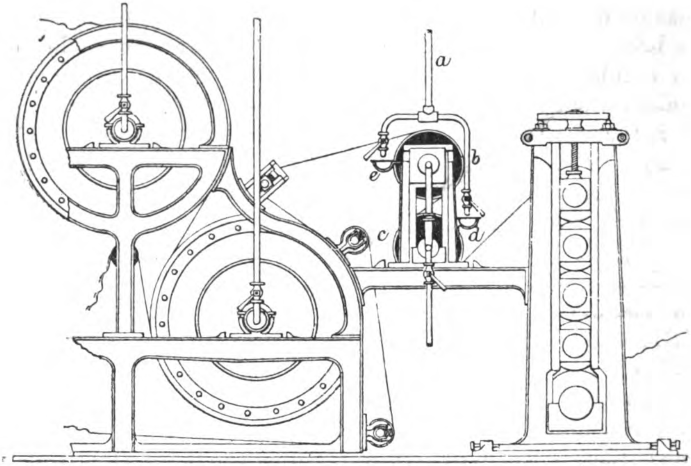

FIG. 54.

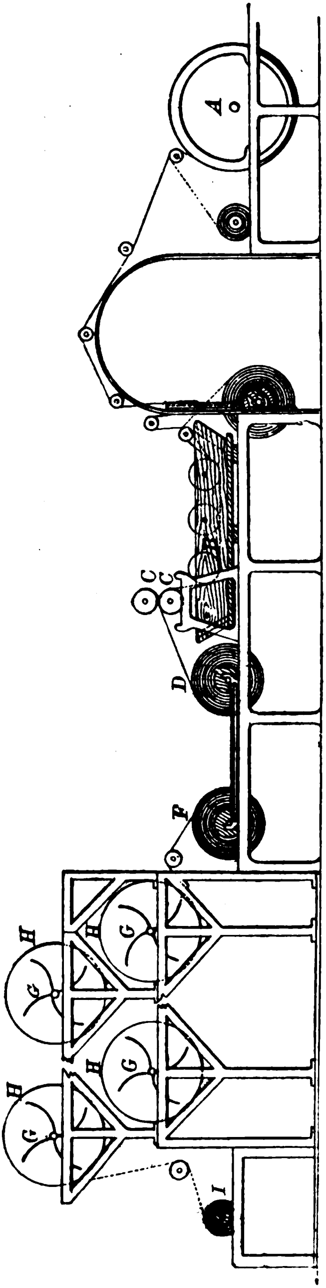

Fig. 55.

in one or other of the vessels containing it. The paper passes between a pair of rollers placed in a trough and dipping into the size. The size may be made to flow through a pipe pierced with a number of holes, the stream running directly on to the web of paper. In the other, and perhaps most general way, at least for the better qualities, the paper is wound off immediately after leaving the last drying-cylinder A (Fig. 55), and sized at some future time, or it may be passed directly into the vat B containing the size. After passing between the squeezing-rolls C, it is generally wound off as at D; and after having stood some time to allow the size to be evenly absorbed by the paper, it is wound off from F, and passed over the cylinders H, of which there may be a very great number, some machines having over 300 of them. These cylinders are made of light spars of wood; inside them, and revolving rapidly in an opposite direction, are the fans G. The paper in travelling over these drums, is only slowly dried, and is supposed by this means to be more perfectly sized, and increased in strength. It is wound on to reels again at I. Only the first and last two drums are shown. This method was devised to imitate, as far as possible, the sizing process of hand-made paper. Even now, paper that has been made on the machine is sized by hand, after having been cut into sheets, much in the same way as hand-made.

Preparation of Size.—Very pure gelatine can now be obtained in the form of colourless sheets. It is, however, more economical for the paper-maker to prepare his own: this is therefore done in the majority of cases. A great many animal substances, such as clippings of hides, horns, bones, &c., yield gelatine when heated with water. Any of these substances may be used, the first being the chief raw material. They are first softened by soaking in cold water for some days: they are then cleansed by washing in a stream of water. The next operation is that of heating with water. This is usually done in iron or copper vessels provided with a false bottom or outer jacket, into which steam may be passed. The hide cuttings are covered with water, and the mass gradually raised to a temperature of about 85° (185° F.). In from ten to fifteen hours nearly the whole of the cuttings will have passed into solution as gelatine. This solution is then drawn off and any insoluble substance suspended in it is removed by subsidence or filtration. The hides contain a certain quantity of fat, which collects on the surface of the solution. The residue in the boiler is again heated with water, and the solution added to the bulk. It is of the greatest importance that too high a temperature be avoided, as gelatine is liable, when strongly heated with water, to lose its power of gelatinising.

To the filtered solution of gelatine, which should be, if properly prepared, of a pale colour, a quantity of alum solution is added. The effect of alum upon gelatine is very remarkable. If added slowly it will be found gradually to render it stiff until at a certain point the mass will become almost solid; a further addition renders it fluid again. It is in this state ready to be used for sizing purposes. The amount of alum necessary to produce this effect is about 20 p.ct. of the weight of the raw material. The alum is also useful in preventing the decomposition of the gelatine, but its chief characteristic is to render the gelatine a more efficient sizing material. There is no doubt that, besides its action upon the gelatine itself, it has a considerable effect upon cellulose. It is of the greatest importance that the alum or the sulphate of alumina, which can be substituted, should not contain any free acid. This is especially necessary in the case of papers made from rags, in the bleaching of which an acid has been used; one effect of which is to remove all basic substances derived from the boiling or bleaching processes. In the case of esparto and similar fibres, a considerable quantity of such substances are present in the pulp, the result being that the free acid of alum is to a large extent neutralised, and its injurious effects prevented.

The effect of the free acid is seen in the weakening of the paper and the destruction of metal surfaces with which it comes in contact. The effect of acid upon cellulose will be found more fully described in p. 13.

Many paper-makers add to the gelatine a certain quantity of soap, the effect of which is to render the paper capable of taking a high finish. The soaps employed should be white and firm, and should be free from rosin. Some soap-makers prepare a special soap for paper-making. They are usually made from tallow, or a mixture of this with a small quantity of cocoanut oil.

If a solution of soap be added to one of alum, a double decomposition immediately occurs, the fatty acid being thrown down in combination with the alumina, and the soda combining with the sulphuric acid. If, however, the soap solution be previously mixed with a solution of gelatine, no precipitation takes place, the mixture forming an emulsion having somewhat the appearance of thin milk.

Various attempts have from time to time been made to size paper in the engine with gelatine, by precipitating it in the pulp after the manner of rosin sizing, but as yet no successful method has been devised.

Single-cylinder Machines.—Modified forms of the original Fourdrinier machine have been introduced to meet various requirements. One suitable for the manufacture of very thin paper, or of papers one side only of which is required to be glazed, called a single-cylinder or Yankee machine, is shown in Fig. 56.

It resembles the Fourdrinier machine as far as the couch-rolls A and B. The paper is taken off the wire-cloth on to an endless felt running round the upper couch-roll A, and travelling in the direction of the arrows. It is taken from the felt on to the large drying-cylinder C, of about 10 feet diameter, heated with steam. This is carefully turned and polished so as to impart a high gloss to the surface of the paper with which it is in contact. Calender-rolls are sometimes supplied in addition.

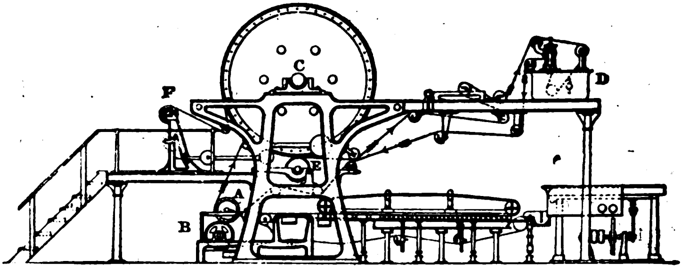

FIG. 56.

The arrangement shown at D is for the purpose of washing the felt. This is necessary to cool and open it out after passing between the cold press-roll E and the hot cylinder.

The paper, after passing over the greater part of the surface of the cylinder, is sufficiently dried, and it is then wound off at F.

A machine of a very different construction from the ordinary form is shown in Fig. 57. The pulp, after passing through the strainer A, enters the vat B, in the centre of which a large drum or cylinder C revolves. This cylinder is covered with fine wire-cloth, and on it the paper is made. As it revolves the fibres attach themselves to the wire, and the water passes through the meshes, being assisted by means of a pump. The sheet of paper thus formed is taken on to the endless felt passing round the couch-roll D, and travels along with it to the large drying-cylinder E, heated by steam. It leaves the felt at F, and is then taken on to the cylinder, after travelling round which it is sufficiently dried, and is then wound off as at G. The felt on its return journey passes through the washer H, where it is cleaned and freed from adhering particles by the scraper I. It is squeezed free from excess of water by the rolls K. Paper made on such a machine is weaker than that made in the ordinary way, because it has not been found possible to give a shaking motion to the cylinder, and thus the fibres are only imperfectly felted.

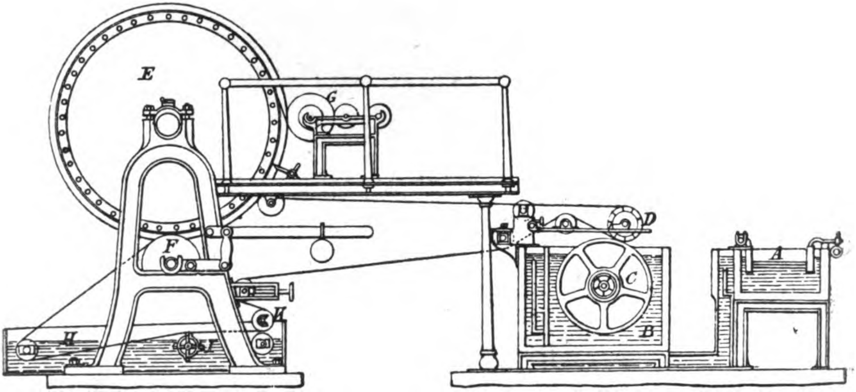

FIG. 57.

A modification of this machine is used for making mill-boards, the difference being that it has no drying-cylinder.

The felt carrying the paper passes between a pair of press-rolls, which squeeze out the water. The sheet of paper is then allowed to wind round the top press-roll until of the required thickness. When this happens, it is cut off the roll by a knife. The thick sheets so produced are dried either in the open air or in a room heated for the purpose.

CHAPTER X.

CALENDERING, CUTTING, ETC.

THE paper, as it leaves the machine, is for many purposes not sufficiently highly glazed, and it is therefore necessary for it to undergo a further process of calendering. This may be done in various ways.

One method, called "web glazing," is to pass the paper between a number of rolls, alternately of polished iron and very highly compressed paper or cotton. The construction of such a calender will be understood by reference to Figs. 58 (end elevation) and 59 (front elevation). The reel of paper, as taken from the machine, is shown at A (Fig. 58), its course over the rolls being indicated by arrows. After passing over the bottom roll, it is wound off on a wooden or hollow iron cylinder B (Fig. 58), driven by the toothed wheel shown by the dotted line C, on the same shaft as the wheel D, which is driven by E, keyed upon the bottom roll. The whole machinery is driven by the large toothed wheel F (Figs. 58 and 59), which is itself driven by the small wheel G on the main shaft H. The paper rolls are marked P, and the iron rolls I. It will be seen that there are two paper rolls in the middle, for the purpose of, as it were, reversing the paper, and so making both sides alike. Pressure is applied to the rolls by means of the screws K, and by the weight L (Fig. 58) acting on the compound lever M. The brake, which consists of a strap of leather, pressing, by means of the weight and lever N, on the circumference of the wheel O, connected by toothed wheels with the cylinder A on which the paper is wound, is used for the purpose of preventing the paper from leaving the cylinder too rapidly.. But for this appliance, the paper would be apt to crease. The paper rolls have an inner core of iron, the paper only extending to a depth of about 5 inches.

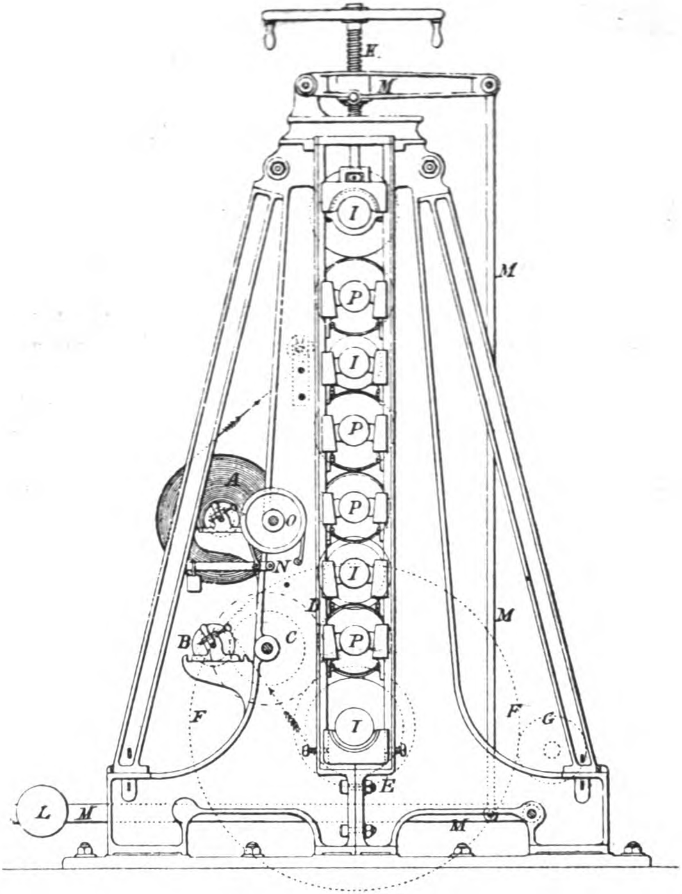

FIG. 58.

The iron rolls are hollow, and are connected with steam-pipes, by which they can be heated.

Another method, known as "friction-glazing," employed for giving a very high finish to paper, generally on one side

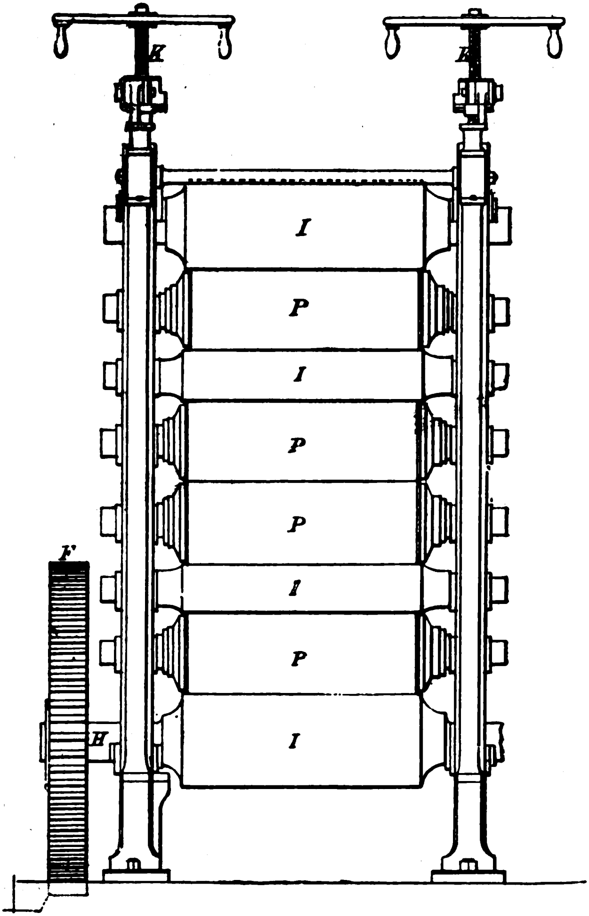

FIG. 59.

only, is to pass it between a large paper roll and a smaller iron one, the latter revolving at a much greater speed than the former. By this means a very smooth surface can be obtained. It is sometimes assisted by rubbing a small quantity of bees'-wax on the small iron roll. The above-mentioned methods apply to the glazing of paper in the web. Paper cut into sheets may also be treated in the same way. Various modifications of these calenders have been devised; they do not, however, involve the application of any special principle. Plate-glazing, a method that is adapted to hand-made and the better qualities of paper, consists in applying heavy pressure to sheets placed between polished plates of copper or zinc. The metallic plates and the sheets of paper are made into bundles, and the whole is passed between two strong rolls, heavy pressure being communicated to them by means of screws or levers, and weights applied to the ends of the upper roll.

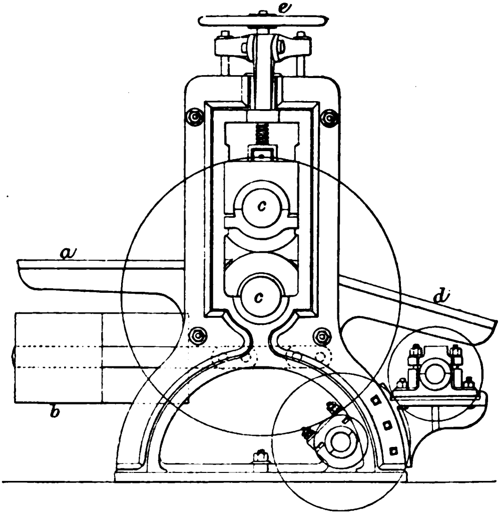

FIG. 60.

A calender for this purpose is shown in Fig. 60. The bundle of plates and paper is passed along the table *a*; after passing through the rolls *c*, it slides along the inclined table *d*, where it is received by a workman. The pressure on the rolls is regulated by the handle *c* and the weights *b*.

By passing paper between rolls on which devices have been cut, the 'repped' and other similar papers are produced.

With calender rolls of the ordinary construction, as the pressure is applied at the extreme ends, the roll is liable to assume a slightly curved shape, the effect of which is to produce an uneven surface on the paper, the outer portion of the web being more highly finished than the centre.

This defect is obviated to a very large extent by Schurmann's Patent Anti-Deflection Rolls (Fig. 61). The roll proper consists of an outer shell *a*, through the centre of which and securely wedged in at *b* is the centre core *c*, the ends of which run in journals, and to which pressure is applied in the usual way. The pressure is communicated to the outer shell at the point of contact *b*, the result being that the parallelism of the surfaces of the rolls is maintained, and, in consequence, the paper tends to be equally finished in every direction.

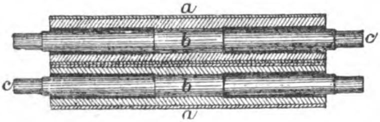

FIG. 61.

Cutting.—Except for special purposes, such, for example, as for use in a continuous printing machine, paper is usually sent from the mill in the form of sheets. The form of cutter, called a revolving cutter, generally used, is shown in Fig. 62. The paper from the webs A is drawn forward by the rolls B; it is then ripped into widths of a convenient size by means of two circular knives, the upper one of which is shown at C. It again passes between a pair of rollers, after leaving which it meets a knife D fastened to the revolving drum E, and pressing against a fixed knife not shown. The cut sheets then fall upon the endless travelling felt F. The action of the knives will be understood by reference to Fig. 63. The edges of the two knives are shown at A and B. The knife B has a slot, in which the bolt D slides, and it is kept in position by means of a spring. This spring causes the knife to slide back slightly as it comes against the fixed knife A. The position of the paper is shown by the dotted line C. The knife B is set on the drum not quite horizontally, so that one end meets the stationary knife a little before the other, thus acting in every respect like a pair of scissors. Fig. 64 shows a pair of ripping-knives. The upper one A is kept in position against the lower one B by means of the

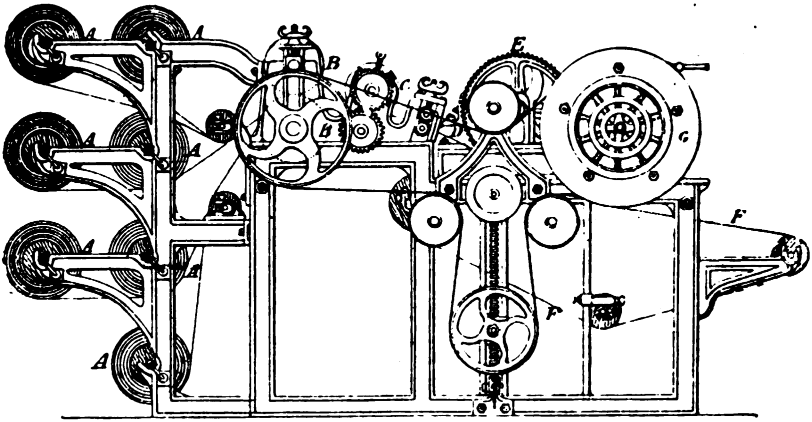

FIG. 62.

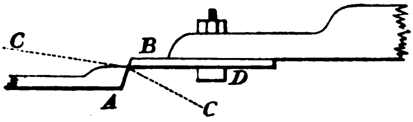

FIG. 63.

spring C. The cutting surfaces are slightly hollowed out, so as to have a sharper edge. The paper is shown by the dotted line D. By altering the relative speed of the drum E and the rolls B, by means of the expanding pulley G, sheets of any desired size can be cut. The cutting-knives are sometimes placed inclined to the drawing-in rolls B, so that the sheet, instead of being cut into a rectangle, is cut into a rhomboid. Such paper is used chiefly for the manufacture of envelopes, this shape occasioning a smaller loss when the envelopes are cut out.

Single-sheet Cutter.—It is sometimes necessary, as in the case of paper having a water-mark, that the sheet should be cut with great exactness, so that the device shall come exactly in the centre. The ordinary cutter cannot be relied on for this purpose, and, in its place, a machine called a 'single sheet cutter' is used (Fig. 65). It consists essentially of a large wooden drum A, fixed on a horizontal axis, over which the paper is led by a pair of drawing-in rolls B. The paper is held against the drum by a clamp worked by the arm C. The paper is cut by the knife E moving against the stationary knife D. After the cut, the drum describes part of a circle, the paper being still held, so that it cannot go back with the drum. As soon as it has gone far enough, the clamp is removed, and the drum returns, bringing the paper with it. The length of the arc through which the drum moves, and

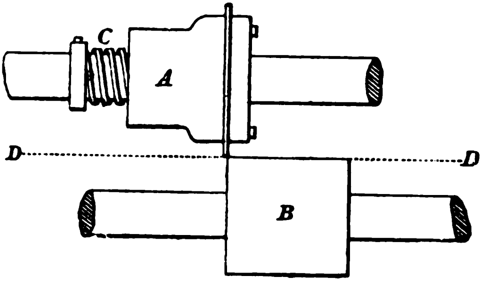

FIG. 64.

therefore the size of sheet, is regulated by the length of the crank-arm F. If from any cause the cut should not take place at the right time, the man in charge can, by pressing against the clamp, retard the motion of the paper, and thus bring back the cut to the right place. The small roller G is for the purpose of keeping the paper always tight.

Guillotine Cutter.—It is sometimes necessary to trim the edges of sheets of paper or to divide them into smaller sheets.

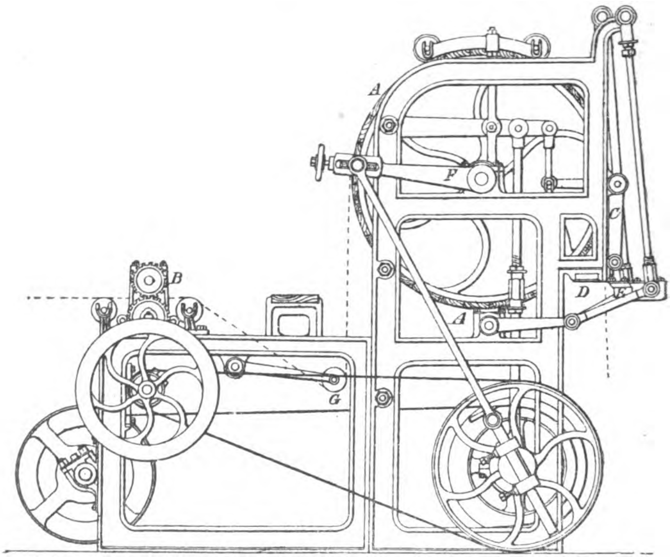

FIG. 65.

This is done by means of a guillotine cutter, an improved form of which, as manufactured by Salmon of Manchester, and called the 'Victory' cutter, is shown in Fig. 66.

The paper to be cut is placed on the table F, touching the back gauge G, which can be brought backwards or forwards by means of the handle H, thus regulating the size of sheet.

The machine is set in motion by means of the lever A, which acts upon a friction-clutch connected with the driving-gear. This causes the knife-bar B and the clamp C to descend. When the latter meets the paper its progress is arrested. The knife D, however, continues to descend, and passes through the sheets of paper. By means of slots placed at the back, the knife is made to take a diagonal course. The pressure of the clamp is maintained upon the paper during the cutting operation by means of a powerful spring contained in the tube E.

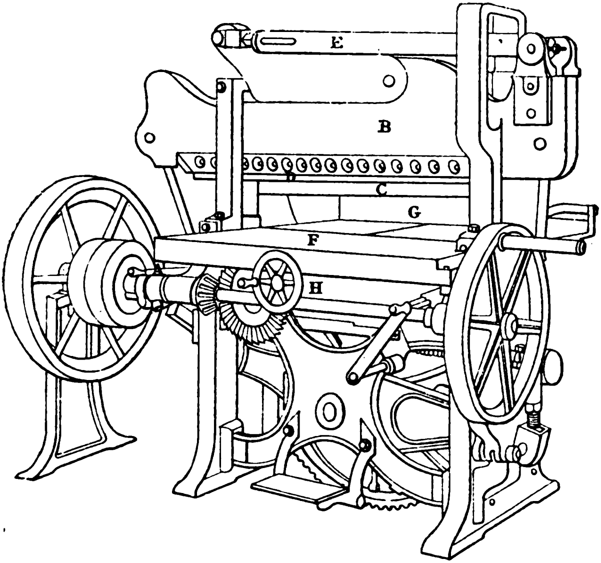

FIG. 66.

Sorting.—The sheets of paper are now ready to be examined before being finally sent away from the mill. This is done in the 'Finishing-house,' or 'Salle' as it is sometimes called. This sorting is usually performed by women, who reject the inferior or damaged sheets. These are sold at a reduced price under the name of 'retree.'

Paper is sold in sheets of definite sizes, and is made up into reams containing from 480 to 516 sheets. These sizes correspond to different trade names—such, for example, as crown, demy, royal, imperial, &c. The weight per ream is usually expressed in addition to the name, thus: 14–lb. demy, 18–lb. double crown, &c. In this way the consumer is enabled to make a rough comparison of the thickness of the different kinds of paper.

In making paper it is the duty of the machineman to examine and weigh from time to time a sheet of the desired size, in order to ensure uniformity. Special lever balances can be obtained, showing at a glance the weight per ream of different numbers of sheets.

The following are some of the sizes of sheets as generally specified for writing and printing papers:—

	Writings.	Printings.
Foolscap	17 × 13¼	17 × 13½
Post	18¾ × 15¼	—
Demy	—	22½ × 17¾
Royal	—	25 × 20

It is particularly in dealing with such quantities as the above sizes and weights of papers that we become aware of the arbitrary and cumbersome nature of our English weights and measures. It is not for us to argue the question of the superiority of the metric system, but to admit it. Apart from the simplicity of calculations based upon the decimal system of units, there is the more important simplification of ideas in a notation based upon *related* quantities. Thus the ton on the metric system is the weight of the cubic metre of water. The English ton on the other hand is related to the yard or unit of length, for all practical purposes, as the dimensions of a ship are to the names of the crew!

In the weight-measure specification of papers on the metric system the weight per square metre in grammes is a measure from which we pass by an instantaneous process to relative thickness of all papers having the same specific gravity: or by direct measurement of thickness, to the relative gravities of papers which vary in this respect.

The paper maker in the mill should adopt some uniform standard—preferably the metric system, having reference solely to the physical constants of paper as paper. The arbitrary and conventional weight-sizes of the stationers' trade may be calculated in terms of the systematic standard which should give a direct and simple universal expression to thickness and specific gravity.

CHAPTER XI.

CAUSTIC SODA, RECOVERED SODA, ETC.

As we have already pointed out, lime and caustic soda are the only alkalis generally employed by the paper-maker for boiling fibrous raw materials; the special cases in which carbonate and sulphide of soda is used have been mentioned in their proper place.

Lime—the oxide of the metal calcium or CaO—is prepared from 'limestones' of varying quality and is also therefore a somewhat variable product. The unavoidable impurities are water, carbonic acid, silicious matters and residues from the coal used in 'burning' the limestone.

The lime should slake readily and the resulting hydrate ($CaO.H_2O$) should form a voluminous impalpable powder.

The preparation of milk of lime requires little or no description, as the operation is a simple and tolerably familiar one. Before using, it should be passed through a fine wire sieve, to keep back sand, coal, and similar impurities which the lime invariably contains.

Caustic soda is prepared by makers who work on the Leblanc system, in various forms, differing from each other in alkaline strength and colour, and of course in price. The lowest quality is what is known as caustic 'bottoms': it consists of that portion remaining at the bottom of the caustic-pot after the clear fused caustic soda has been ladled out, and it contains a considerable quantity of ferric oxide and other insoluble impurities. It is of a dark reddish brown colour, and contains 50–60 p.ct. of alkali (Na_2O). Its use in paper-making cannot be recommended, except for the preparation of the very lowest grade of pulp. The solution should be allowed to remain at rest, in order that the insoluble matter may subside.

The next in quality is known as cream caustic, so called from its slightly brown colour. It is usually sold containing 60 p.ct. of alkali, in the form of a tolerably friable mass, having a crystalline structure. It is a convenient form of alkali for the paper-maker.

The next in order is what is called 60 p.ct. white. It consists of a hard white mass, requiring considerable force to break it. Though whiter in appearance than cream caustic, it is in reality less pure, as it contains a considerable quantity of salt. It is made by continuing the evaporation of the caustic liquor to a further point than is the case with cream caustic, the result being that the whole of the water is driven off. A small quantity of nitre is then added to oxidise the sulphides and other compounds which impart the colour to cream caustic. Common salt is then added to reduce its strength to 60 p.ct., in order to satisfy the trade, which convention insists upon an article of a given definite strength. On this account it is somewhat inferior to cream caustic, and is, moreover, more expensive.

A higher quality is white 70 p.ct. This resembles white 60 p.ct. in appearance, but is much purer, and more expensive.

The following analyses of different forms of caustic soda and their relative prices will possibly be of interest :—

	(Davis.) White (70 per cent. Na_2O).	(Davis.) White (60 per cent. Na_2O).	(Morrison). Cream (60 per cent. Na_2O).
Sodium hydrate	89·60	75·25	70·00
„ carbonate	2·48	2·53	5·00
„ chloride	3·92	17·40	7·00
„ sulphate	3·42	4·40	2·00
„ sulphide	0·02	0·03	..
„ silicate	0·30	0·30	..
„ aluminate	trace	trace	..
Water	none	none	15·80
Insoluble matter	none	none	0·20

Their relative prices per ton f.o.b. Liverpool, in December 1886, were:—70 p.ct. white, 8*l.* 5*s.*; 60 p.ct. white, 7*l.* 5*s.*; 60 p.ct. cream, 7*l.*

The following are the results of more complete analyses of trade samples, carried out in the authors' laboratory:

Caustic from Spicers (Hunt & Co.).

$NaOH$	72·39	= Na_2O 56·11
Na_2CO_3	6·25	= Na_2O 3·65
Na_2S	—	——
$Na_2S_2O_3$	2·90	59·76
Na_2SO_3	1·13	
Na_2SO_4	1·00	
$NaCl$	9·44	
Na_2SiO_3	1·08	
$Na_2Al_2O_4$	·99	
Fe_2O_3	·21	
$CaSO_4$	·27	
MaO	·03	
H_2O	4·31	
	100·00	

Caustic from N. W. Paper Co. (Muspratts), February 1889.

$NaOH$	72·155*
Na_2CO_3	8·225†
$NaCl$	8·470
Na_2SO_4	2·378
Na_2SO_3	3·340
SiO_2	0·200
Al_2O_3	2·780
Fe_2O_3	·180
Water, &c. (diff.)	2·272
	100·000

* From litmus test, this includes ½ Na_2O as Na_2SO_3, also Na_2O as Silicate.
† Diff. between litmus and ph. ph.

"*Bottoms*" *from McMurray, March* 31, 1890.

Litmus	63·8	Al_2O_3	5·0
Ph.	63·4	Na_2SO_3	0·3

All the above-mentioned forms of caustic soda occur in the form of more or less hard masses, and are contained in thin wrought-iron drums, which are filled with the caustic in a fused state. The soda is removed by breaking the drum with a chisel and hammer. The lumps of caustic may be put direct into the boiler, though it is better to dissolve them previously in water and allow any insoluble impurities to settle to the bottom of the solution.

At the present time there is a considerable industry in concentrated solutions of caustic soda: Solutions containing 30–40 p.ct. NaOH. Thus 'pure liquor 90° Tw.' is quoted to-day (December 31, 1898) at *3l.* *15s.* per ton. Also there is a considerable supply of much purer forms of solid caustic soda, such as are made by causticising 'ammonia soda.' The relative prices current we may note as under:

	£	*s.*	*d.*
77 p.ct. Caustic soda	7	12	6
74 " "	7	7	6

Instead of buying caustic soda direct, it is the custom of some paper-makers to prepare it for themselves from carbonate of soda, which can now be obtained in various forms, some of great purity.

It occurs as caustic ash, containing about 40 p.ct. of alkali as carbonate, and about 10 p.ct. as caustic soda; soda-ash containing about 52 p.ct. total alkali, nearly all as carbonate; and refined soda-ash containing 57–58 p.ct. of alkali as carbonate. Some forms of carbonate of soda, such, for example, as those made by the "ammonia process," (Solvay) are of even greater purity. The method of converting sodium carbonate into caustic soda will be described subsequently.*

Unless the arrangements for washing and draining the lime-mud are very perfect, it is probably cheaper for the paper-maker to buy his caustic direct from the maker.

Ferric Oxide Causticising Process.

The principle of this process is the expulsion of the carbonic acid from sodium carbonate by ferric oxide at high temperatures; this oxide playing the part of a weak acid, entering into a loose combination with the soda, which is overcome by water in the subsequent lixiviation process,

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* For a fuller discussion of these questions, see 'The Economy of pure Caustic Soda,' a paper by the Authors in J. Soc. Chem. Ind., 1889.

the ferric oxide being regenerated and a solution of caustic soda obtained.

The ferric oxide is therefore continuously available. The main features of the process, disregarding the question of commercial economy, are (1) that it leaves no by-products to be disposed of, (2) that it enables the manufacturer to produce directly, without evaporation, a highly concentrated caustic lye.

Soda Recovery.—In former years, the liquors in which rags, esparto, and other paper material had been boiled, was run into the nearest watercourse; but now, owing partly to the fact that is insisted upon by the Rivers Pollution Act of 1876, and partly because it can be made remunerative, all these liquors are preserved, and the soda they contain utilised. The method adopted is to evaporate to dryness and ignite the residue. The soda during the process of boiling takes up a large amount of non-cellulose fibre constituents and dissolves them as resinous compounds. These on evaporation and ignition become converted into sodium carbonate. From the previous account of the boiling processes it will be seen that in many cases one-half the organic matter of the original passes into solution in the alkaline lye. The calorific value of this organic matter is considerable, and its combustion therefore under regulated conditions may be made to furnish the greater part of the heat required for concentration of the liquor to the firing point. Many raw materials, especially esparto and straw, contain a large amount of silica, a large proportion of which is dissolved by the soda in the form of sodium silicate, in which form also it is found in the recovered soda.

The apparatus for accomplishing the evaporation varies with almost every mill. In some, it is very primitive and crude, consisting perhaps of only a furnace for incinerating the residue, and over it a pan containing the liquor, the latter being heated and evaporated by the heat from the furnace. It is obvious that, with such an arrangement, a large quantity of heat must be wasted. To economise as much as possible of this waste heat, various plans have been suggested. That of Rœckner, of Newcastle, appears to be to a great extent

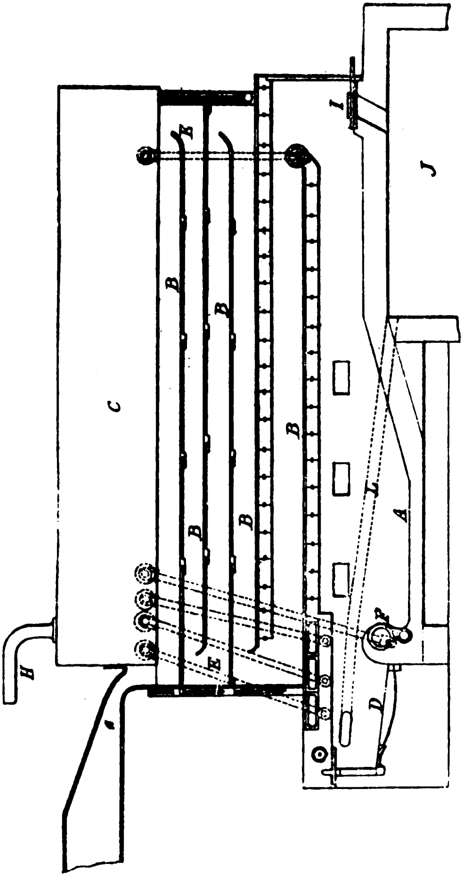


FIG. 67.

efficacious. It consists practically of a series of shallow trays B (Fig. 67) placed in a brick chamber, alternated so as to allow the heated air from the furnace below to play upon the surface of each in succession, on its way to the chimney, with which the whole system is in connection. Above the chamber containing these trays, is a large tank C, containing a store of the liquor to be evaporated, placed there so as still further to economise the heat, and from which the liquor runs on to the trays. The furnace A is of the ordinary reverberatory kind; below it, and connected with it by a kind of damper, is a large chamber J, where the calcined residue from the furnace is put to cool, thus preventing any nuisance from the smell of the burning mass. The chamber is provided with a pipe L, through which the vapours pass into the furnace. Several pipes E from the furnace pass through the tank, to assist in warming the liquor. The residue, when cold, is drawn through doors from the chamber below the furnace. Rœckner has devised an apparatus (Fig. 68), consisting of a small chamber containing a series of pipes A, through which a stream of cold water constantly runs, in connection with the flue from his evaporator, for the purpose of condensing volatile bodies, and thus preventing, to a certain extent, contamination of the surrounding air.

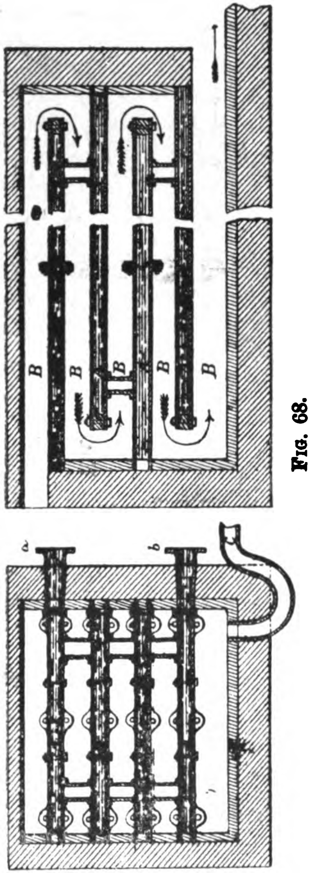
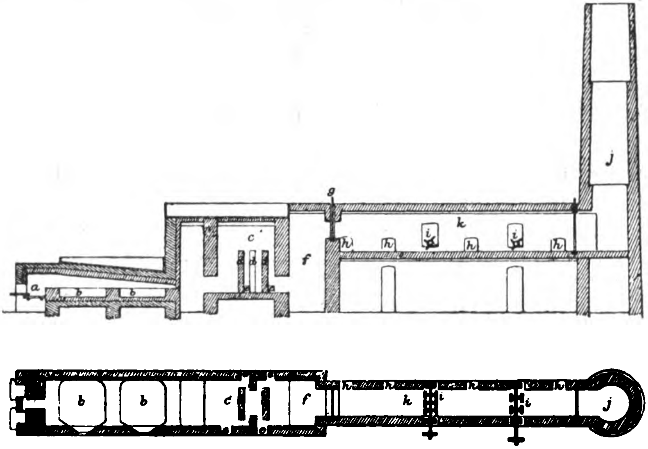


Fig. 68.

A very economical form of evaporator is that invented by Porion, a French Distiller, and named after him. It is shown in sectional elevation and plan in Figs. 69 and 70. It is largely used on the Continent, and also in England and Scotland. It consists of a large chamber *k*, the floor of which is slightly inclined from the chimney shaft, and through which the waste heat from the furnace *a* passes.

The liquor to be evaporated is run in at the end nearest the chimney from the tank placed above the chamber *c*. A number of cast-iron fanners *i*, dip into the liquor and revolve rapidly, usually at the rate of about 300 revolutions per minute, producing and filling the chamber with a very fine spray, thus presenting a very large evaporating surface.



FIGS. 69 and 70.

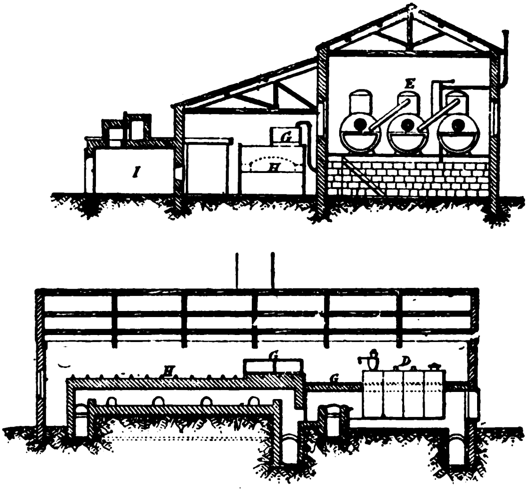
Between the furnace and the evaporator are placed the chambers *c* and *f*. In *c* a number of brick walls *d* are so placed that the flames from the furnace are intercepted and broken up. The object of this is to give time for all the products of combustion to be thoroughly burnt up, which would not be the case without the 'smell-consumer,' as these chambers are called. This part is an addition to the original evaporator, and was devised by Messrs. Menzies and Davis. The liquor after having been concentrated in the chamber *k* runs into a trough placed alongside the doors *h* and flows into one or other of the furnace beds *b* where it is still further concentrated, and the residue ignited by the flames from the fires *a*. The draught can be regulated by the damper *g*, and also by one placed near the shaft *j*. The doors *e*, in the smell-consuming chamber, are for the purpose of cleaning out. The fanners *i* are worked by a small steam engine, not shown in the drawing. Under properly regulated conditions very excellent results can be obtained with this evaporator. The temperature of the gases near the chimney should not be higher than about 85°. By running the fanners at a very high speed the temperature of the gases may be even further reduced, thus showing the completeness of the evaporation.

This form of evaporator is open to the objection that the whole of the sulphur in the coal employed for the furnaces, finds its way into the recovered soda. It combines with the alkali to form sulphite of soda, part of which is decomposed in the furnace with formation of sodium sulphate, sulphide, and other sulphur compounds. The same objection, of course, applies, though perhaps in a less degree, to all systems of evaporation in which the flame is in contact with the liquor to be evaporated.

The Porion evaporator can be erected at very small cost and costs but little for maintenance. It is capable of producing $\frac{3}{4}$ ton of recovered soda per ton of coal with liquors of the usual strength. It has proved itself to be perhaps the most economical evaporator existing.

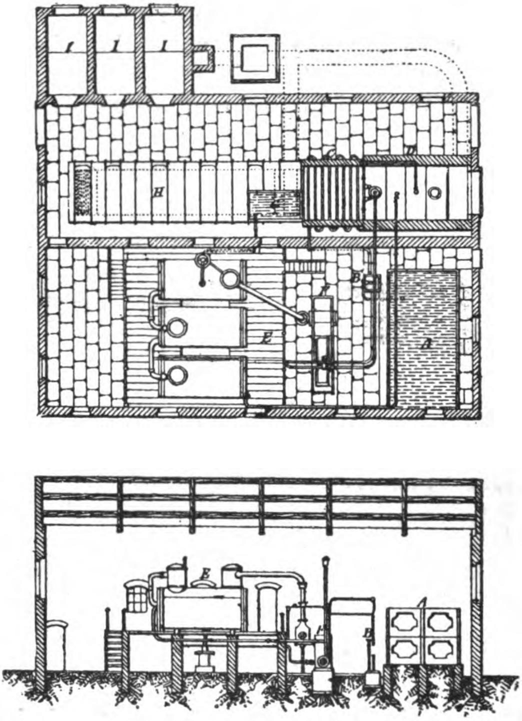
Some time ago there was erected in Lancashire an evaporator invented and patented by Mr. Alfred Chapman. It is shown in Figs. 71, 72, 73, and 74. The evaporation is effected at a low temperature in three vacuum pans E, and with the unusual result that the concentrated liquor gelatinises after leaving the third vacuum-pan, instead of taking the ordinary form of the concentrated products of other evaporators. It is said that this apparatus gives an excellent product, with great economy of labour and water, and with no drainage of foul liquor from the buildings. Observations extending over three months have proved that it evaporates 22 lb. of water from the liquor per lb. of coal used under the boiler. It is however very costly to erect.

The waste liquor is discharged into the tank A, whence it



FIGS. 71 and 72.

is pumped by the donkey-engine B, through the feed-heater C, into the boiler D, which receives heat from the incinerating furnace H, and, in case of need, from an auxiliary furnace shown on the plan, under the feed-liquor-heater. The steam produced in D is taken to the first vacuum-pan at E, and having heated its contents, the products of evaporation pass over into the tubes of the second pan ; this, in its turn, gives up its products of evaporation to the third, whence they go to the condenser of the vacuum-engine F. Thus the heat from the furnace H is used for incinerating the concentrated liquor on its bed, for heating the feed-liquor in the feed-heater pipes, and for making steam out of the liquor itself in the boiler; this steam finally drives the donkey-pump and vacuum-engine, and causes the evaporation in the three vacuum-pans E. One advantage of this evaporator is the fact that the liquor is evaporated out of contact with the furnace gases.



FIGS. 73 and 74.

"*Evaporation by Multiple Effect.*"

In recent years there has been a large development of methods of evaporation based upon the ideal of an exhaustive utilisation of the heat expended upon the liquors to be concentrated. The principle of these methods is that of 'multiple effects,' which may be briefly explained as follows:—A liquid is converted into vapour under ordinary conditions of boiling, by overcoming the pressure of the atmosphere upon its surface. The quantity of heat required to vaporise, as also the temperature of the ebullition, will be less as the pressure to be overcome is less. Further, the vapour continuously driven off carries with it a quantity of heat, which is its heat of condition or latent heat. This heat it imparts to any colder body (e. g. a further quantity of the same liquid) with which it comes in contact, direct or indirect; if the quantity of the latter be relatively small, it will raise its temperature approximately to that of the ebullition of the first liquid. If now the pressure (atmospheric) on the surface of the latter be slightly reduced, by any means, it will boil. The vapour from this can be made to boil a third quantity of the liquid, under a further diminished pressure.

The successive effects in economic evaporation consist, therefore, in utilising the latent heat of a vapour given off from a liquid under a certain pressure (e.g. that of the atmosphere) to vaporise a further quantity of the liquid under a pressure maintained by mechanical means below that of the first. In certain methods the vapour does its work in the successive effects by passage through systems of tubes, the liquid to be heated being in contact externally; in the Yaryan system, on the other hand, the arrangement is reversed. The liquid to be evaporated traverses the system of tubes which are heated externally by the vapours. At the end of each effect, the liquid is caused to impinge, in a special chamber, upon a disc: in this way a complete separation of liquid and vapour is effected, each then passing on to the next effect, the former through the tube-system, the latter to the chamber inclosing these. The flow of liquid is maintained by a force-pump, and the diminished pressure by a vacuum-pump suitably disposed. This system differs from that described on p. 252, in that the evaporation is continuous, the dilute liquors entering the apparatus and the highly concentrated liquors leaving it in an unbroken stream. The rate of flow is such that the evaporation of the caustic liquors from wood boiling from 8–10° to 80° Twaddell, in a quadruple effect, requires only a few minutes. At the latter concentration it is ready for the incineration process, which by means of a rotary furnace, such as that of Mr. J. W. Hammond, of the firm of S. D. Warren and Co., is also effected continuously. It is found, moreover, that the excess of heat available from this process is sufficient for the evaporation.*

Whatever be the method of evaporating or concentrating the liquor, the final treatment in the furnaces is much the same in every case. The furnaces shown in Figs. 69 and 70 may be taken to represent the ordinary form. The concentrated liquor is run on to either of the beds *b*, where the last portions of water are driven off by the heat from the fireplaces *a*, and the residual mass is ignited until all the organic matter contained in the liquors is carbonised and the soda is converted into carbonate of soda. This takes place in about 4 hours, according to the degree of concentration of the liquor as it is run into the furnaces. The running in of liquor should be done with great care, as explosions sometimes occur through the sudden liberation of steam on the liquor coming in contact with the hot beds. The charge should be allowed to remain in the furnace until it is thoroughly carbonised and all volatile matters have been driven off, otherwise a nuisance may be caused when the still burning mass is exposed to the air. Rœckner's evaporator is provided

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* A full account of these methods is given by Griffin and Little, loc. cit. pp. 165–170. The student may also consult a treatise by J. Foster on "Evaporation by the Multiple System," London: Simpkin, Marshall and Co., 1890.

with a special chamber into which the charge is drawn (J, Fig. 67).

The composition of the recovered soda varies with the nature of the liquors from which it has been obtained, and, as has been already pointed out, with the form of evaporator employed. It consists essentially of carbonate of soda, together with a certain amount of silicate of soda, if derived from liquors in which straw or esparto have been boiled, chloride of sodium, sulphate of soda, sulphite of soda, sulphide of sodium, and other sulphur compounds, the rest being made up of carbon and insoluble impurities. The amount of soda varies from 35 to 45 p.ct. (Na_2O). The following analysis will give some idea of the composition of Recovered Soda:—

			Na_2O
*Sodium carbonate	72·33	=	42·306
Sodium hydrate	1·93	=	1·497
Sodium chloride	8·30		———
Sodium sulphate	3·95		43·803
Sodium sulphite	·63		
Silica	7·09		
Carbon	4·70		
Oxide of iron and alumina	·50		
Other constituents (by difference)	·57		
	100·00		

The whole of the soda present as sulphur compounds is not lost, as a large proportion of it is present as sodium sulphite, most of which is converted into caustic soda by the causticising process.

A certain amount of soda is carried forward, partly mechanically and partly volatilised, to the flue leading to the chimney. This accumulates, and may be from time to time removed in the form of fine dust. It contains, besides carbonate of soda, much sulphate and chloride. In two different samples examined by the authors, the amounts of soda (Na_2O) present were 25·0 and 27·1 p.ct.

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* A certain quantity of potash derived from the mineral constituents of esparto and straw is always present in recovered soda.

Causticising.—The next process consists in converting the sodium carbonate in the recovered soda into caustic soda.

This operation is known as 'causticising,' and consists in heating a solution of the soda with lime. The decomposition which takes place is shown in the following equation:—

Sodium Carbonate.		Lime.		Water.		Caustic Soda.		Calcium Carbonate.
Na_2CO_3	+	CaO	+	H_2O	=	$2NaOH$	+	$CaCO_3$

It must be remembered that this is a reversible reaction and that caustic soda will attack calcium carbonate under certain conditions of concentration and temperature, to re-form sodium carbonate and lime. Hence the limits of decomposition, which have been determined by G. Lunge as follows:—

P.ct. Na_2CO_3 in Liquor.	Sp. gr. before Causticising.	P.ct. Soda Causticised.
2	1·022	99·4
5	1·052	99·0
10	1·107	97·2
12	1·127	96·8
14	1·150	94·5
16	—	93·7
20	—	90·7

The recovered soda should be dissolved in separate vessels. Perhaps the best form of apparatus is a series of lixiviating tanks such as are used for dissolving the alkali in black ash. By this means a nearly perfect exhaustion of the mass can be effected with a minimum of labour. Special tanks are sometimes made for the purpose, provided with mechanical stirrers.

It is essential in dissolving the recovered soda that a high temperature should be employed, as otherwise a portion of the soda present as silicate of soda will be lost, as it is only with difficulty soluble, and requires rather prolonged heating with water. Whatever the form of apparatus employed it should be so arranged that, after running off the strong liquor, the insoluble residue may be further treated with water. In the case of the vats mentioned above, this process is made continuous, pure water being run in at one end, and strong liquor flowing from the other. If other forms are used, the liquor after settling, may be run off by means of a pipe passing through the bottom or side of the vessel, and near the bottom and consisting of two parts, one long and one short. The short part is stationary, and is connected to the longer part by means of a movable knee joint, allowing it to be deflected. The liquor having settled sufficiently, the movable limb is lowered beneath the surface of the liquor which is then allowed to flow through. As the surface of the liquor falls, the pipe is gradually lowered. In this way the clear solution can be run off without disturbing the residue at the bottom. The open end of the pipe is usually covered with coarse wire gauze, to keep back insoluble impurities. With properly calcined recovered soda, the solution should be bright and almost colourless. If at all brown in colour, and if it has an empyreumatic odour, it indicates imperfect calcination. The residue in the dissolving tanks consists chiefly of carbonaceous matter, together with some soda, insoluble matter, &c.

The liquor is now ready to be causticised. This should be done in a separate vessel, although it is the practice in many mills to perform this operation in the same vessel in which the solution of the soda has been conducted. A good form of causticiser can be made from an old egg-shaped boiler, by cutting it in two along its length.

It should be provided with two or more vertical steam pipes, connected at the bottom of the boiler with a horizontal pipe perforated with numerous holes. The vertical steam pipes should be furnished with injectors, whereby air is drawn in, and forced with the steam through the holes in the horizontal pipe. The stream of air serves the double purpose of thoroughly agitating the liquor and of oxidising any sodium sulphide in the recovered soda. The liquor before causticising should be reduced in strength to about 20–25 degrees Twaddle, which may be done with the washings of the residue from the recovered soda, or from the washings obtained subsequently from the lime-mud. This strength should never be exceeded, otherwise imperfect conversion into caustic soda is the result. This is due to the fact that concentrated solutions of caustic soda react upon calcium carbonate, forming sodium carbonate, and calcium hydrate, the reaction being the reverse of that indicated in the above equation. If the liquors are very strong in carbonate of soda, and comparatively free from sulphate, they should not be causticised at much over 20° Twaddle, if they contain much sulphate, and therefore less carbonate, the higher strength can with safety be adopted.

The causticising vessel should be provided with a stout iron cage or basket, into which the lime can be put. This should be securely fastened to the vessel, and should dip into the liquid.

The liquor having been properly diluted, is now heated by means of the steam pipes, and the lime put into its cage. It should be put in in lumps. As the liquor reaches the boiling point, the reaction will proceed rapidly, and the lime will gradually disappear; fresh lumps should be added if necessary. If the liquor is sufficiently heated the causticising will be complete in from two to three hours. The liquor should be tested from time to time; this is usually done by a workman. He withdraws a sample of the liquor, and after allowing the calcium carbonate to subside, pours off a portion of the clear liquid into a glass vessel. He then adds an excess of either sulphuric or hydrochloric acid. If any effervescence takes place, due to the evolution of carbonic acid gas, he knows that the operation of causticising is incomplete; the heating must therefore be continued. It is difficult, without an undue expenditure of time and steam, to convert the whole of the soda into caustic: it should however be so perfect, that on testing only a very slight effervescence occurs. It is quite easy to convert as much as 95 p.ct. of the soda, or even more (see p. 258). The actual amount converted can only be ascertained by a careful analysis of the liquor.

The amount of lime used is generally somewhat in excess of the theoretical quantity; 106 parts of sodium carbonate (Na_2CO_3) require 56 parts of lime (CaO): it is necessary, however, to add about 60 parts. A very good plan is to conduct two or even three causticisings in the same vessel without cleaning out or removing the calcium carbonate, using in the first operation a large excess of lime. The causticising being completed, the calcium carbonate and excess of lime are allowed to settle down, and the clear liquor run off by an arrangment such as that already described in the dissolving process. Fresh solution is then run in and the whole mass heated for some time, until the excess of lime is converted into carbonate. Fresh lime is then added if necessary until the conversion of the carbonate of soda is complete. The liquor is then allowed to settle, and is run off as before: this operation may again be repeated.

The residual calcium carbonate, or 'lime-mud' as it is called in alkali works, is then washed once or twice by running in water, boiling up, allowing to settle, and running off the clear liquor. If these liquors are too weak for use in boiling fibres, they may be used for diluting fresh recovered soda liquor before causticising, or for dissolving the soda.

Some arrangement should be provided for removing as much as possible of the liquor from the lime-mud before throwing it away or otherwise disposing of it. This is best done by throwing it on a filter made of layers of stones, ashes and sand, and covered at the top with perforated iron plates. The filter is connected with a vacuum pump. In this way very perfect drainage is accomplished, and the mud forms a hard mass on the surface of the filter, from which it can be easily removed with spades. In this form it contains only 50–60 p.ct. of water. If properly washed it should contain in this state only about 2 p.ct. of alkali (Na_2O). By careful manipulation, even this amount can be reduced.

The importance of thoroughly washing the mud can hardly be too much insisted upon. Where proper means are not employed for draining, the washing should be made more perfect. The lime-mud consists chiefly of carbonate of lime, together with silicate, free lime, &c. The following analysis is of a mud obtained by causticising recovered soda derived from the liquors in which esparto and straw had been boiled:—

Calcium carbonate	40·02
Calcium hydrate	5·13
Silica	4·01
Sodium hydrate	2·13
Oxide of iron and alumina	0·30
Water	48·10
Other constituents	0·31
	100·00

As already pointed out the liquors contain a certain amount of soda, as sodium sulphide and other sulphur compounds. The presence of the former, if in large quantities, is objectionable, as it is liable to discolour fibres boiled in liquors containing it. It is therefore best to remove it. This can be conveniently done by blowing air into the liquors during the process of causticising: this has the effect of oxidising it to sulphate of soda, in which form it is harmless.

The air can of course be blown into the liquor by means of a pump; the most economical way is to connect with the steam pipe an injector constructed on the principle of the injectors used for feeding boilers and for other purposes. By this means a strong current of air is drawn in, and being forced with the stream to the bottom of the liquor, passes through it in a number of fine streams.

If the amount of sulphide present be very high it may be necessary to prolong the oxidising operation beyond the time necessary for complete causticising.

In many paper-mills the causticising is conducted in circular vessels furnished with mechanical agitators. These are more expensive than the simple form described above, and they possess no special advantages. The use of causticisers in which neither mechanical agitation nor agitation by means of air is provided for is exceedingly wasteful of labour, time, steam, and soda. The lime-mud settles at the bottom as a [illegible] mass, very difficult to manipulate.

CHAPTER XII.

PAPER TESTING.

There are two points of view from which a paper may be tested: first, of physical or mechanical properties; secondly, of material composition. We shall consider the subject according to this division.

(1) Quantitative measurements of such properties as resistances to breaking and tearing strains are seldom made by English paper-makers. In Germany, on the other hand, the matter has been very thoroughly investigated in connection with the work of the Königl. Techn. Versuchsanstalt, Berlin, and through the agency and influence of Prof. Sell and C. Hofmann, a department has been organised exclusively for the work of paper testing. The results of the tests are becoming widely recognised by practical men and the trade in that country, as affording a true index of the quality of a paper. It is therefore of importance to give an outline of the method employed.

The determination of the strain or weight which a paper is capable of supporting is a very obvious measure of the strength of the paper. Observations of the limiting strain or breaking weight are sometimes made by paper-makers, but the apparatus and method employed are usually crude. The simplest means consist in clamping the paper—a strip of standard length and breadth, arbitrarily chosen—at one end, the clamp being firmly held in a fixed support, and to the other attaching by means of a similar clamp, an ordinary scale pan, the whole arrangement hanging vertically. Into the pan, weights are added in due succession until fracture of the strip is determined. It is scarcely necessary to point out that the errors of experiment with such a method are very great: indeed it has been found that even with the refined apparatus about to be described the errors are not inconsiderable. However, by exhaustive investigation, according to the well-known 'law of errors,' these have been quantified, and a careful operator can therefore obtain results which are trustworthy. The apparatus in question is the Hartig-Reusch machine.* It is shown in sectional elevation and plan in Figs. 75 and 76.

The principle will be readily grasped by inspection of the diagrammatic representation of its essential parts—Fig. 77. The strip of paper is held horizontally by the clamps *a* and *b*, *a* being held by the fixed support A, *b* by the movable carriage B. B is connected by means of a swivel with the spiral spring F, and this again is similarly connected with the screw, which is made to rotate by the wheel D. By turning D, therefore, the spiral may be extended, and a corresponding strain communicated through B and *b* to the paper. The paper undergoes a certain elongation under the strain, and the carriage B moves from right to left in consequence. The rotation of the screw is continued, and the extension of the spiral proceeds until the paper is fractured. At this point it is required to determine, (1) the elongation of the spiral which is the measure of the breaking strain, and (2) the distance through which the carriage has moved, i. e. the elongation of the paper. Both these effects are communicated to the pencil G, the latter directly, since the pencil-holder is in rigid connection with B, the former through the rod I, from which by a special arrangement, the horizontal is converted into a vertical motion of the pencil. This, therefore, traces a curve, of which the ordinates represents the strains, and the abscissæ the elongations of the paper produced by the strain.

The scale shown in Fig. 76 indicates the exact position of the clamp A.

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* A complete description of this machine is given in 'Civil Engineer,' 1879.

Fig. 75.

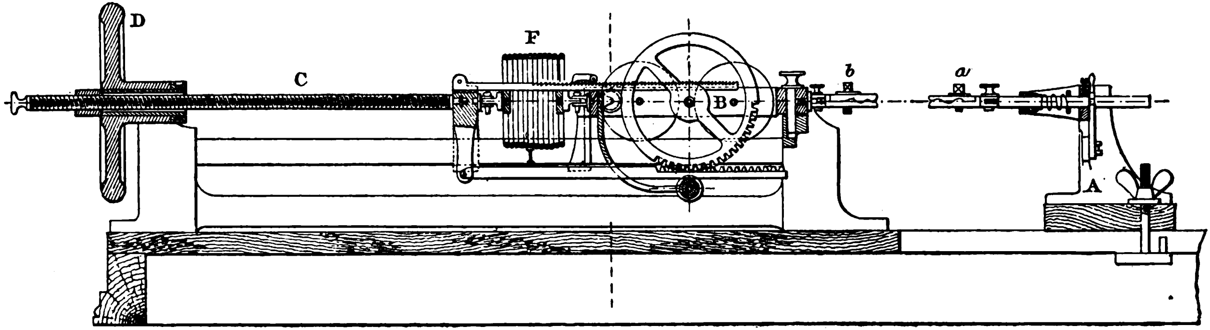
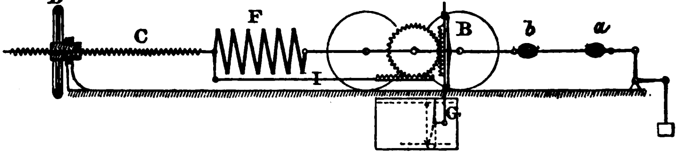


Fig. 77.



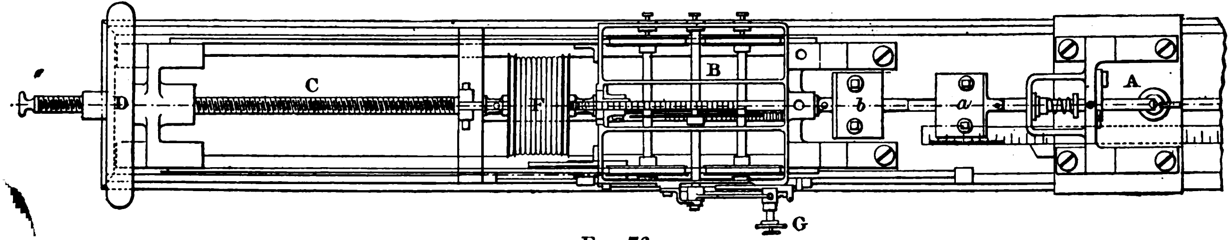


Fig. 76.

The values for the spiral spring—i. e. extension for a given load—having been determined by previous observations in a special apparatus, the curve obtained is at once a measure and a permanent record of these cardinal factors, breaking strain and elasticity. As with all other such instruments, the recording apparatus introduces certain errors, which, however, by careful investigation and modification in accordance with the results, have been reduced to a minimum. Nevertheless, the director, Dr. Martens, has recently adopted a simpler instrument, altogether similar in principle, but based upon a direct reading of the two movements, in which of course these errors do not appear. For the student, however, the recording instrument is the more instructive, and we have given it preference for description here, more especially as no difference in essential parts is involved.

Those who wish to pursue the matter into the most interesting details of the investigations made upon the subject, are referred to the papers published by the Institute for 1885. A useful abstract of these publications so far as relates to paper, has been made by the Society of Arts Committee on 'The Deterioration of Paper,' and published in the report upon that subject.*

In testing the strength of papers by this or similar machines, it is important to observe the hygrometric state of the atmosphere at the time the trials are made, as this has been found to exert a considerable influence on the results, a paper being weaker the moister the atmosphere.

The results of the tests are expressed in the following terms:—The elongation is given directly in percentage of the original length. This is uniformly taken at 180 mm., a length arrived at after laborious investigation, as minimising the errors of experiment; in other words, as giving mean value with the minimum of variation. For the breaking strain an ingenious expression has been arrived at,

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* Journ. Soc. Arts, 1898.

viz. the length of the paper which suspended vertically, with one end hanging freely, the other fixed, would determine fracture at the fixed end. As the breaking strain would vary with the thickness, the numbers obtained in units of force or weight for strips of constant breadth, would need correction in order to admit of strict comparison with one another. By substituting an expression in terms of the paper itself—since a paper of greater thickness and requiring therefore a proportionately greater force to fracture it, weighs more per unit of area, and in the same proportion—all the numbers for breaking strains are strictly comparative one with the other. In the same way also the question of width may be disregarded.

A further mechanical test, forming a part of the scheme of investigation, is the resistance of the paper to rubbing. This test is an altogether empirical one, as the following brief description will show:—A piece of the paper, about 6 inches square, crumpled by successive folding in two directions at right angles, is grasped by the thumb and forefinger of each hand, at a distance of 3 to 4 inches apart. It is then rubbed upon itself across the thumbs a given number of times (seven is the number chosen) and held up to the light. If no holes are visible, the rubbing is repeated. The number of times necessary to repeat the rubbing until holes appear is the measure of the resistance. A sufficient uniformity in the results of this test has been observed to make it the basis of a classification of papers, in regard to their resistance to such disintegration; they are divided into the following seven groups, beginning with the lowest:—

0. Extremely weak.
1. Very weak.
2. Weak.
3. Medium.
4. Moderately strong.
5. Strong.
6. Very strong.
7. Extremely strong.

The classification of papers on the results of these tests cannot be more lucidly given than in the following scheme, under which the results are officially recorded:—

Class	1	2	3	4	5	6
a. Mean breaking length (metres) not less than	6000	5000	4000	3000	2000	1000
b. Mean elongation (p.ct.) at fracture not less than	4·5	4	3	2·5	2	1·5
c. Resistance to rubbing	6	6	5	4	3	1

This classification is based on the results of some hundreds of observations. It is interesting to note the differences observed in the numbers for *a* and *b* according to the direction in which the paper is cut for the test, i. e. in the direction in which it was run on the paper machine, or at right angles, i.e. across the web. The mean ratio for the breaking lengths (strains) may be taken as 1 : 1·6, i. e. the paper is about 40 p.ct.* weaker across the web; the elongation under strain on the other hand is about double.

It may be pointed out that resistance to strains applied as in the testing machine, is not a full measure of the strength of a paper as shown in actual use. Thus it does not give full value to the influence of length of fibre, which is an important factor of resistance to shearing or tearing strains. This quality is measured roughly by the paper expert, by tearing the sheet in the two directions, noting the kind of tear and the tearing force which he employs.

It is also of interest to note the influence of the glazing process (p. 235) upon the quality of the paper as determined by these tests.

First, we must notice the effect of the treatment upon the substance of the paper itself. The mean reduction of thickness is 23 p.ct. On the other hand, the reduction of weight, calculated per unit of surface (square metre), is 6·7 p.ct., whence we may infer an increase of surface, flattening out, in the process. These quantities, but more particularly the latter, will doubtless vary with the various methods of glazing and with the materials of which the paper is composed.

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* In the statement of results the mean of the numbers obtained in the two directions is given.

The breaking length (strain) shows a mean increase of about 8 p.ct.; the elongation under strain, on the other hand, a diminution of 6 p.ct.

For an interesting discussion of the question of the relative strengths of machine and hand-made paper see 'Paper,' by Richard Parkinson.

The thickness of a paper may be determined by means of an ordinary micrometer, such as is shown in Fig. 78. The paper is placed in the jaws of the instrument, and the screw advanced until it touches the paper. The thickness is then read off on the scale. Other forms of apparatus are sold for the same purpose. In making a determination of the thickness of a paper it is necessary to take the mean of a series of observations at different points of the sheet, as the thickness may vary somewhat.

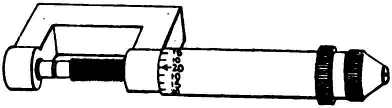

FIG. 78.

The product obtained by multiplying area by thickness, determines the volume or cubic contents of the paper substance: and the weight of the unit of volume being the specific gravity, this constant is readily deduced. 'Bulk' as currently expressed, is the inverse of this, i. e. volume per unit of weight. In every mill it is important to keep records of the numbers expressing this quality.

Special papers.—Such as are used for some special property, are tested with particular reference to that property. Thus blotting papers are tested by their relative capacities for absorbing and transmitting fluids. Strips of the paper are cut of constant and equal length, and suspended vertically. The lower extremities are then inserted in a vessel of water, and the time is noted during which the water rises to a constant height, also the extreme height to which the water rises by capillary transmission is also noted.

Determination of Composition of Papers.

(II.) The analysis of a paper naturally divides itself into two parts:—(*a*) The determination of the nature of the fibrous material of which it is composed; and (*b*) the identification of such adventitious substances as size and filling material.

(*a*) This again is divided into two sets of observations—microscopical and chemical.

A fragment of the paper is soaked for some time or boiled for a short time in dilute alkaline solution, and is then carefully teased out with a pair of needles, and the fragments laid on a glass slip with a drop of diluted glycerine. A cover-glass is then laid on and lightly pressed down so as to spread the fibres in a thin layer.

The microscopical features of the different fibres have been already described, and it is only necessary now to summarise the chief characteristics of the more important materials.

Cotton.—Flat riband-like fibres, frequently twisted upon themselves. The ends generally appear laminated. The fibres are frequently covered with numerous fine markings (see Frontispiece).

Linen.—Cylindrical fibres, similar to the typical bast fibre (see Fig. 6). The ends are frequently drawn out into numerous fibrillæ (see Frontispiece).

Esparto.—Esparto pulp consists of a complex of bast fibres and epidermal cells. These serrated cells are, as has been already pointed out, characteristic of esparto, straw, and similar fibres. Certain differences exist between those of esparto and straw, and even between the different species of straw, which enable the microscopist to identity their source. The most characteristic feature of esparto pulp is the presence of a number of the fine hairs which line the inner surface of the leaf (*e*, Fig. 10), some of which invariably survive the boiling and washing processes, although the greater portion passes away through the wire-cloth of the washing engines.

The presence of these hairs may be taken as conclusive evidence of the presence of esparto.

Straw.—Straw pulp very closely resembles esparto-pulp in its microscopical features. The hairs above alluded to are, however, absent. On the other hand, a number of flat oval cells are always present in paper made from straw (*b*, Fig. 13). It should be borne in mind, however, that bamboo and similar pulps also contain these cells.

Wood (Chemical).—Flat riband-like fibres, showing unbroken ends (see photographs, Frontispiece), The presence of the pitted vessels (Frontispiece, and *a*, Fig. 15) is eminently characteristic of pulp prepared from pine-wood. The fibres of other woods are not sufficiently characteristic. They much resemble those of pine-wood, with this difference, that the pitted vessels are absent.

Wood (Mechanical).—Mechanical wood-pulp may be recognised by the peculiar configuration of the torn ends of the fibres, and from the fact that the fibres are rarely separated, but are generally more or less agglomerated (see Frontispiece). Pulp from pine of course shows the pitted vessels already referred to. They are usually more distinct than in chemical wood-pulp. Occasionally fragments are to be met with connected together with portions of the medullary rays.

The identification of the ligne-cellulose is rendered very certain by previously staining the specimen with a basic-aniline dye, or with the phloroglucol reagent (p. 85), or with a solution of a salt of aniline or dimethyl p. phenylene diamine.

The microscopical examination of a paper is a matter of very great difficulty, and one requiring much practice. The student is recommended to study closely for himself the microscopical features of pulps obtained from authentic specimens.

A fair measurement of the relative proportion of the various fibres present in a paper can be obtained from a careful microscopical examination.

Vétillart * was the first to maintain that a quantitative determination within a fair limit of accuracy is possible.

The degree of accuracy attainable depends first upon the kind of mixture under examination, and secondly, upon the experience of the observer.

In examining a paper under the microscope, it should be observed whether the fibres appear as fragments, or whether they consist of whole (bast) cells in which the tapered ends appear.

Cotton and linen, owing to the great length of their ultimate fibres, yield, when beaten, fragments showing where the fracture has taken place. From the appearance of this fracture it is possible to ascertain whether or not the beating operation has been properly conducted. If the beater-knives have been too sharp, or have been let down to the bed-plate too quickly, the fractures will appear as clean cuts, whereas when the operation has been properly conducted the fracture will appear ragged and drawn out. The bearing of this on the strength of the finished paper is considerable.

Esparto, straw, and wood, whose ultimate fibres do not exceed 1–2 mm., should, in the majority of cases, appear as whole (bast) fibres with two tapered ends; the beating, when properly conducted, being confined merely to the separation into these ultimate fibres.

(*b*) For the chemical identification of the fibres in writing and printing papers, the most useful reactions are those with aniline sulphate solution. The fibres (celluloses) of the rag and wood groups give no reaction, but straw and esparto celluloses and mechanical wood-pulp can be identified by its means. The authors have found that when a paper containing straw or esparto is treated for some time with a boiling 1 p.ct. solution of aniline sulphate, a red colour is produced. Esparto gives the reaction with greater intensity than straw. In this way the presence of a very small quantity of these pulps can be detected with certainty. Since esparto and

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* Études sur les Fibres Vegetales Textiles, Paris, 1876 (Firmin-Didot).

straw cellulose give large yields of furfural in boiling with hydrochloric acid of 1·06 sp. gr., a determination of furfural gives a close approximation to the proportion of these celluloses in a paper containing only linen and cotton celluloses in addition. The percentage is obtained by multiplying the furfural number by 8.*

Mechanical wood-pulp, when treated with a solution of aniline sulphate, develops, even in the cold, a deep yellow colour. If a paper containing mechanical wood-pulp so treated be examined under the microscope, the fragments of wood will be found to be deeply stained, whereas the other fibres remain colourless or nearly so. It must be borne in mind that cellulose obtained from lignified fibres, if the boiling and bleaching processes have not been carried sufficiently far, will give with aniline sulphate a more or less intense yellow coloration. Various other reagents have been suggested for the identification of mechanical wood-pulp, all based upon the production of a colour with lignose. Of these the most important is the solution of the coal tar base, dimethyl p. phenylene diamine, the reactions of which have been previously described.

The reaction of lignose with chlorine and sodium sulphite solution already referred to (p. 54) may also be made available for the detection of mechanical wood-pulp in a paper. Imperfectly boiled or bleached pulps sometimes give this reaction faintly.

Quantitative Estimation of Mechanical Wood-pulp.—The determination of the amount of mechanical wood-pulp present in a paper is sometimes a matter of some importance, and it is also a matter of some difficulty. A general idea of the amount present can be obtained by observing the depth of the yellow colour produced with aniline sulphate or the intensity of the magenta reaction with chlorine and sodium sulphite. Wurster's colour reactions (supra) are more pronounced and the quantitative findings based upon them are

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* For details of furfural estimation see 'Cellulose.'

generally accepted as affording a sufficiently close approximation. Test papers containing the diamine base together with a scale of colours corresponding to varying percentages of the lignocellulose, are obtained from Schuchardt of Görlitz (Germany). It is also possible to calculate approximately the percentage from the percentage of cellulose contained in the specimen. Mechanical wood-pulp (pine) may be taken to contain 60 p.ct. of cellulose. If, therefore, a paper ascertained to contain a pure cellulose in addition to this constituent, yield 75 p.ct. of cellulose on the ordinary test, it may be assumed that about 62·5 p.ct. of mechanical wood-pulp is present.

The authors have proposed a method of estimating the amount of mechanical wood-pulp present in a paper, based upon the absorption of iodine in definite proportions by wood in a finely divided state, under strictly regulated conditions. The paper is carefully reduced to a fine pulp and is then left in contact with a standard solution of iodine in potassium iodide. At the end of twenty-four hours the amount of free iodine is determined by titration with sodium thiosulphate and by deducting this from the amount originally taken, the amount absorbed is ascertained. As this amount, under strictly comparative conditions, always corresponds to a definite amount of mechanical wood-pulp the amount present can be readily calculated.

2. *Loading, Sizing Materials, &c.*—The determination of the amount of loading material in a paper has been already described (p. 201). The identification of the material can only be arrived at by a careful chemical analysis. The principal loading materials are china-clay and pearl-hardening (calcium sulphate), and in coated or 'art' papers, barium sulphate. The ash from a paper containing china-clay is insoluble in boiling dilute hydrochloric acid; that from paper containing calcium sulphate is soluble: the solution on cooling deposits long needle-shaped crystals of $CaSO_4 2H_2O$ (20·93 p.ct.) and gives with barium chloride a copious precipitate of $BaSO_4$ (barium sulphate) insoluble in acids,

and with ammonia and oxalate of ammonia a precipitate of calcium oxalate. To examine for barium sulphate the ash is fused with a mixture of sodium and potassium carbonate. The mass is boiled out with water.

The presence of starch in a paper can be readily ascertained by its behaviour with a solution of iodine. If starch be present the well-known blue colour of the compound of iodine and starch will be produced. The determination of the amount of starch present is a matter of some difficulty, the details of which are somewhat beyond the scope of the present work. It is based upon the conversion of the starch into sugar, and the estimation of the latter with Fehling's solution.

The authors have investigated the removal of starch by the action of saliva. The amylolytic action of this secretion is favoured by a slightly alkaline reaction, and a temperature of 30–40° C. The paper to be treated is treated with boiling water and after cooling to 40° a little sodium bicarbonate is added to slightly akaline reaction, then a small quantity of saliva. With this it is digested 4–5 hours at 30–40° and then washed. The starch is estimated by the loss of weight sustained.

The nature of the material with which a paper is sized may be ascertained in the following way:—

The sample, cut up into small fragments is warmed for a few minutes with absolute alcohol containing a few drops of acetic acid. The alcohol is allowed to cool, and is then poured into four or five times its bulk of distilled water. If any precipitate or cloudiness is produced, it indicates that the paper has been sized with rosin. The alcohol dissolves the rosin, which, being insoluble in water, is thrown down on dilution. The alcohol used may be obtained from commercial spirit by digesting it with lumps of quick lime and distilling from a water bath.

The paper after treatment with alcohol should now be boiled for some minutes with water: the solution allowed to cool, and then filtered. To the filtrate a few drops of a solution of tannic acid are added, when, if the paper has been sized with gelatine, a white curdy precipitate will be formed.

The estimation of the amount of sizing material in a paper is a very complicated process and one which demands considerable chemical experience for its proper conduct.

The amount of gelatine present is best ascertained by determining the amount of nitrogen present by combustion with soda-lime, and from this, calculating the amount of gelatine. Pure gelatine contains 18·16 p.ct. of nitrogen (Muntz). The comparison of one paper with another with a view to ascertain the relative degree of sizing, is usually performed in a more or less rough and ready way by moistening the samples with the tongue for a certain time, and noticing the degree of transparency produced, which is of course inversely to the degree of "hardness." A more accurate method consists in placing a drop of a mixture of alcohol and water containing some colouring matter in solution and determining the time necessary for the colour to make its appearance on the other side. In this way more trustworthy comparisons can be made.

Colouring Matters.—The chemical characteristics of the chief colouring matters have been already described. 'Mineral' pigments will be obtained in the ash, in some cases without chemical change (smalts, iron oxides, &c.), in other cases in the form of the characteristic constituent of the original pigments. Thus the prussian blues leave a residue of iron oxide; the chromates may be more or less 'reduced' to chromic oxide. The coal tar colours and soluble dyes are recognised by characteristic reactions, for which the special test books dealing with the subject must be consulted.

CHAPTER XIII.

GENERAL CHEMICAL ANALYSIS FOR PAPER-MAKERS.

A KNOWLEDGE of the methods usually employed for the qualitative and quantitative analysis of the various chemical substances met with in paper manufacture is of considerable importance. The scope of this work will not allow us to enter fully into the necessary details of manipulation; for these the reader is referred to standard works on analysis: we will merely indicate the methods.

Lime.—In its commercial forms contains in addition to the active calcium oxide, water and carbonic acid, in combination with lime, and substances insoluble in acids, derived partly from the original limestone, partly from the coal used in 'burning' it.

Magnesian limestones yield a lime containing of course magnesia.

These facts indicate the methods to be pursued by the analyst in valuing a sample of lime. Water and carbonic acid may be estimated jointly by the loss of weight on igniting to a white heat in a platinum vessel till constant. Earthy impurities such as sand by treating the lime with a dilute acid in slight excess, filtering off and weighing the insoluble matter. For an exact determination of silica, alumina, iron oxide and magnesia, the usual systematic separation must be followed.

In actual practice it is usual to estimate the lime by a direct volumetric method; a standard solution of oxalic acid being added to the lime previously slaked and brought to the condition of 'milk of lime.' As an indicator, phenol phthalein is used. The reaction is carried out in a stoppered bottle, which is vigorously shaken from time to time. The oxalic acid solution is added until the pink colour of the phthalein is discharged.

Caustic Soda, Soda Ash, Recovered Soda, &c.--These substances are always valued by the amount of real alkali (Na_2O) that they contain, which is determined by titration with a standard acid.

In testing recovered soda, it is necessary to *boil* the finely powdered ash for some time with water; unless this be done, the amount of alkali will probably be under-estimated, as part of the soda is present as a difficultly soluble silicate.

It is sometimes desirable to determine the amount both of sodium hydrate and carbonate in a sample of alkali. For this purpose an excess of a solution of barium chloride is added to a solution containing a known quantity of the substance under examination, and the mixture made up to a definite volume. It is then filtered, and an aliquot portion of the filtrate titrated with standard alkali. The filtrate contains only the alkali that was originally present as hydrate, the carbonate of soda having formed with the barium chloride, insoluble barium carbonate, and sodium chloride.

Bleaching Powder.—The value of bleaching powder depends upon the amount of 'available chlorine' that it contains. This is determined by means of a standard solution of arsenious acid. The standard solution is prepared by dissolving pure arsenious oxide (As_2O_3) in sodium carbonate solution. To test the powder, a quantity, say about 5 grms., is taken, and is carefully ground up in a mortar with a small quantity of water, more water is then added, and the coarser particles allowed to settle for a few seconds. The milky liquid is then run off into a graduated flask; the residue is again ground up with water, and the operations repeated until the whole of the powder is transferred to the flask. The flask is now filled up to the proper mark, carefully shaken, and an aliquot portion withdrawn as quickly as possible.

It is necessary to take both the soluble and insoluble portions in order to obtain uniform results. Standard arsenious acid solution is now run in until the solution ceases to produce a blue colour with iodide of potassium and starch papers.

A very rapid and satisfactory method is that of causing the bleaching powder to liberate its equivalent of iodine from potassium iodide in presence of hydrochloric acid, using sufficient excess of the iodide to dissolve the titrated iodine completely. The iodine is then titrated in the usual way with a standard solution of sodium thiosulphate.

The method of estimating the amount of available chlorine in bleaching powder by determining the quantity of ferrous sulphate it is capable of oxidising is fallacious, as by this means calcium chlorate is included in the result.

In bleaching powders of low strength this test becomes, however, of value as a measure of the spontaneous decomposition of the powder causing loss of 'available chlorine.' The 'chlorate' strength may be taken as the difference between the numbers for total oxidising chlorine and available or hypochlorite chlorine.

Bleaching powder should contain about 35 p.ct. of available chlorine, but the percentage frequently falls below this amount, especially in warm weather.

Great care should be exercised in the sampling of bleaching powder, as indeed of all chemicals, in order to insure an average result. Small portions should be taken from different parts of the bulk; the whole should then be carefully mixed, and, if necessary, reduced to powder. Portions of the mixture should be taken, pounded, and again thoroughly mixed.

If this process be repeated once or twice, a perfectly uniform sample will be obtained.

Alum, Sulphate of Alumina, Alum Cake, &c.—The points to be considered in an examination of such of these products as are perfectly soluble in water are (1) the percentage of alumina contained in them; (2) the percentage of iron, and (3) the amount of free sulphuric acid present.

(1) The alumina is estimated as such by precipitation with ammonia. Ferric oxide is also thrown down with alumina, and must therefore be deducted from the amount of the mixed oxides obtained.

(2) The percentage of iron oxide present is determined in the following way. A considerable quantity of the sample under examination is dissolved in water, and to the boiling solution a large excess of caustic potash solution is added. The caustic potash precipitates both the alumina and ferric hydrates, the former, however, redissolves. The solution is filtered, and the precipitate of ferric hydrate washed, dissolved in dilute hydrochloric acid, and reprecipitated with excess of caustic potash. It is again thrown on to a filter, washed, redissolved in hydrochloric acid, and again reprecipitated with ammonia. In this way it is obtained free from alumina.*

An alternative method, to be recommended when the iron is present in larger proportion, is the volumetric process with permanganate: the ferric being reduced to ferrous oxide by reduction with zinc in presence of acid, the latter being then quantitatively re-oxidised by the titrated permanganate solution.

(3) *Free Acid.*—This can be estimated indirectly, i. e. by estimating the alumina and ferric oxide, calculating the amount of sulphuric acid necessary to combine with them, and deducting this from the total amount of sulphuric acid estimated. In the case of alum it is of course necessary to make due allowance for the sulphate of potash or ammonia present. The sulphuric acid is estimated as barium sulphate in the usual way.

An approximate method of estimating free acid consists

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* For a method of estimating minute quantities of iron in alums see 'Journ. Soc. Chem. Ind.,' April 1887, p. 276.

in digesting a weighed quantity of the finely powdered sample in strong alcohol. The alcohol dissolves away the free acid, which can be estimated in the solution by means of a standard solution of alkali.

Free acid can be detected by means of a solution of Congo-red, which is turned blue with free acid, but not with pure sulphate of alumina.

Insoluble Matter is present in greater or less proportion in many of the 'alum-cakes' of commerce. Such constituents are of course destitute of 'alum value.' They are estimated by boiling out the sample with water; collecting, washing, drying and weighing the undissolved residue.

Sizing Test.—Griffin and Little recommend a direct measure of the sulphate of alumina in terms of rosin size precipitated. The following are the practical details of the test as given in their 'Chemistry of Paper-making' pp. 331, 332.

A standard size solution is prepared by dissolving about 25 grammes of good ordinary rosin in about 250 c.c. of strong alcohol. The solution is then filtered from insoluble matter, and diluted with a mixture of 500 c.c. of strong alcohol and 300 c.c. of water to nearly 1000 c.c. A little phenolphtalein in solution is then added, and standard soda solution added drop by drop, shaking after each addition until a faint pink tinge is observed in the solution. This shows that all the rosin acids are combined with soda, and that the solution is one of neutral resinate of soda or neutral rosin size. The solution is now to be made to 1000 c.c. with the diluted alcohol mentioned above, and if not entirely clear, filtered again or allowed to stand until it settles clear. The clear alcoholic solution constitutes the standard size solution.

The value of this solution is next to be determined, best by means of a solution of pure crystallised ammonia alum, one part of which alum we have found to precipitate 2·46 parts of neutral rosin size.

For this purpose the clear, colorless crystals should be coarsely crushed in a mortar, and the resulting powder pressed between two sheets of filtering paper to remove any accidental moisture. Five grammes are then carefully weighed and dissolved to 500 c.c. Each cubic centimetre of this solution will then contain 0·01 gramme of alum.

Two burettes are next filled, one with the size solution, and one with the alum solution.

A flask of 150 to 200 c.c. capacity is filled about two-thirds full of water, and 20 c.c. of the size solution is run into it from the burette. The alum solution is next run in, a few drops at a time the mouth of the flask being closed with the thumb and the flask vigorously shaken after each addition of alum, and allowed to rest until the flocculent precipitate formed has risen clear, which takes but a few moments. The addition of the alum solution should be continued until the precipitate on rising leaves the solution entirely clear, without the slightest trace of milkiness or opalescence.

The number of cubic centimetres of alum × 0·01 equals the amount of ammonia alum required to precipitate the size in the 20 c.c. of standard size employed. This multiplied by the factor for ammonia alum, as above, equals the quantity in grammes of neutral size in 20 c.c. of the standard solution.

The actual test of an alum is performed in exactly the same way; a solution of 5 grammes of the alum to 500 c.c. being employed, and, if necessary, filtered through a dry filter before titrating. 20 c.c. of the standard size solution are always employed, and the actual amount of neutral size it contains having been determined as above, it is easy to calculate from the data given by the titration the amount of size which one part of the alum tested will precipitate.

This test, as is evident, gives the absolute precipitating power of the alum, and does not discriminate between sulphates of alumina iron, or other metallic oxides which may be present, or free acid, all of which have the power of precipitating size.

Antichlor, Sodium Thiosulphate, Sodium Sulphite, &c.—Sodium thiosulphate can be estimated by means of a standard solution of iodine in potassium iodide. The operation should be performed in dilute solution (see p 182).

The same solution serves also for the estimation of sulphurous acid in sodium and other sulphites.

Starches.—After having made a careful microscopical examination of the sample, it should be examined for water by drying at 100° C., and for mineral matter by igniting in a platinum crucible and weighing the residue. The water should not exceed 18 p.ct., and the ash ·50 p.ct. The samples should be carefully examined for insoluble matter by dissolving in water and filtering. It is also useful in comparing different samples of starch to convert the specimens into pastes, under exactly similar conditions.

When perfectly cold, the 'stiffness' of the pastes should be compared. This may be done by noting the relative resistance to weights placed upon their surface. Information on this subject is contained in a paper by W. Thomson in the 'Journ. Soc. Chem. Ind.,' March 1886.

The identification of starches by means of their microscopical appearances is tolerably simple, as each particular kind possesses characteristic differences.

Gelatine.—Samples of gelatine should be examined for water and ash. The water should not exceed 16 p.ct. and the ash 2·7 p.ct. The relative strengths of the jellies formed with water should also be compared. This may be done in the way indicated above for starches.

Raw materials intended for the preparation of gelatine may be similarly examined. They yield the whole of their gelatine on heating with water. The effect of prolonged heating on solution of gelatine should be borne in mind. The amount of residue left after treatment with water should be carefully determined.

Soaps.—The soaps most suitable for use in paper-making are those known as curd and mottled, the former being chiefly used for the fine qualities. They should be carefully examined for free alkali and unsaponified fat. Full descriptions are contained in Lant Carpenter's 'Treatise on Soap-making.'

Dyes, Pigments, Loading Materials, &c.—These substances are best examined from a physical and tinctorial point of view, by comparison with specimens of undoubted purity and excellence.

The chemical examination is both difficult and somewhat misleading. A microscopical examination will often throw much light on their composition.

For comparing the tinctorial power of pigments, weighed quantities should be ground up with starch or some other white powder. In this way the comparison of the intensity of colour is much facilitated.

CHAPTER XIV.

SITE FOR PAPER-MILL, WATER-SUPPLY, WATER PURIFICATION, ETC.

In choosing a spot on which to build a paper-mill, the manufacturer has to take into consideration several very important circumstances. Chief of these is the necessity for having a large supply of water at command. Not only is a large quantity needful, but it should be free from impurities, such as suspended matter and soluble iron. The former, it is true, can be removed by settling and filtration; the latter cannot, and is liable to injuriously affect the colour of the paper. Again, as a question of economy in working, it is advantageous to have convenient water-power; therefore for this, as well as for the former reason, paper-mills are usually situated on the bank of a stream. In choosing such a site paper-makers are probably also influenced by the fact that it affords a ready means for the removal of impurities. In properly conducted mills, where suitable apparatus is employed for evaporating the liquors in which the raw material has been boiled, the stream should not be polluted to any very great extent. Generally speaking, the greater the pollution, the more are valuable materials being lost to the manufacturer. It is obvious that the site for a mill should also be chosen with reference to its proximity to means of transit for the raw and manufactured materials.

The disposition of the different divisions of a paper-mill depends of course upon the nature of the paper it is intended to make and to a large extent upon local circumstances. Fig. 79 will give some idea of the general arrangement of a mill for manufacturing esparto paper.

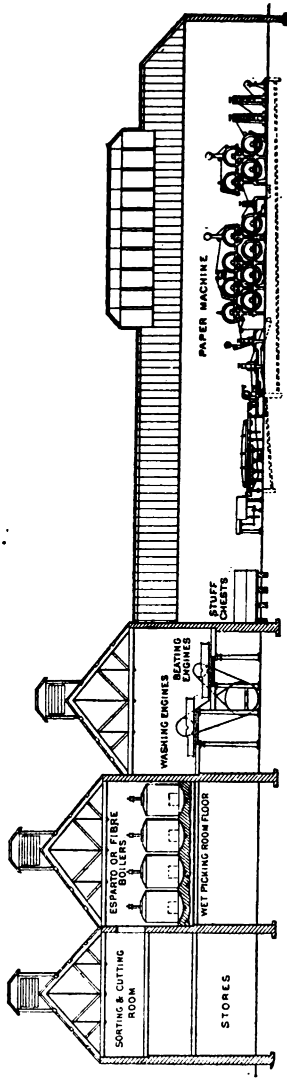

FIG. 79.

Water Purification.—Arnot in his Cantor lectures on the technology of the paper trade states that from 30,000 to 40,000 gallons of water are required for the manufacture of each ton of paper. The importance of a pure and copious supply is therefore very evident.

The impurities of water consist of two classes, insoluble and soluble. The former can be readily removed by processes of settling and filtration. For this purpose most paper mills are provided with large ponds capable of holding several days' supply. These are sometimes supplemented by filtering beds of sand. Insoluble impurities can also be removed by passing the water through filter-presses.

Of late years a number of filters have been devised which, while occupying much less ground space than that occupied by settling ponds and filters, effectually remove the greater part if not the whole, of the insoluble impurities.

Of such we will briefly describe a few typical instances.

Many of these are so arranged that they can be readily cleansed and the collected insoluble impurities removed.

Wilson's Patent Automatic Self-cleansing Filter as manufactured by Messrs. Masson, Scott and Bertram is an example.

Fig. 80 shows a side sectional elevation of the filter with its automatic mechanism. The filter proper is an open top cast iron cistern containing the filtering medium. Above it is a flushing tank containing the water which cleanses the filtering medium of the impurities arrested and accumulated therein, at intervals varying, according to the state of the water being filtered.

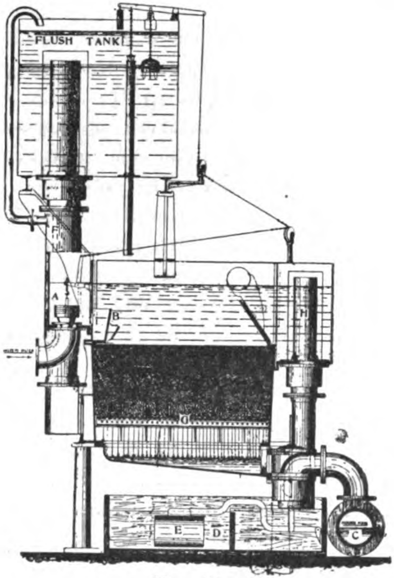

Fig. 80.

Entering through the valve regulating box A, the water passes on to the distributing board B, which runs the whole length of the filter. This serves to distribute the entering water uniformly over the length of the filter. After percolating through the medium it is discharged into the filter main C. This filtering process continues until the medium becomes silted up with impurities, thereby obstructing the free percolation of the water under filtration, which being thus obstructed, accumulates until it rises to a certain level, when it overflows a syphon which draws off a quantity of the water into the float chamber D, sufficient to raise the float E.

The float thus raised closes the inlet and outlet valves, and operates a valve in the flushing tank, by means of which the contents are discharged down the large syphon pipe F, and upwards through the filtering medium by means of a series of perforated pipes. The air occupying these pipes and the spaces in the cellular bottom underneath the filter bed being forcibly ejected by the downrush of water, performs a most important function in thoroughly aerating and agitating the filtering medium, thereby separating it from the impurities, which, being lighter than the medium, are floated upward and drawn off by the large syphon H, into the float box, from which it escapes to a drain.

When all the impurities have been drawn off and have escaped from the float chamber, the float falls, causing the various valves to resume their normal position, and the ordinary operation of the filter is resumed.

This cleansing of the filter, automatic from first to last, occupies from two and a half to three minutes. The quantity of water used for the cleansing operations is, when filtering water containing an average amount of matter in suspension, about 5 p.ct. of the total amount purified, but when filtering waters that are comparatively pure this amount seldom exceeds 3 p.ct. As the interval of time between the washings depends upon the amount of impurities in the water, these filters are very suitable for dealing with waters obtained from sources which are subject to sudden and frequent pollution, and also for the treatment of effluent discharges from works which have to meet the demands of the Rivers Pollution Act.

Greig's Patent Filtering Apparatus (No. 29,070, 1897) consists of a series of closed settling tanks, connected together at the top by pipes and furnished with hopper-like bottom which serves to collect the insoluble impurities, which can be removed from time to time by sludge cocks. The last series of settling tanks is connected with a filtering tank provided with a number of compartments filled with ashes which serves as a filtering medium. These compartments can be removed and replaced by others containing fresh ashes.

This filter is also adapted to the treatment of effluent waters.

The Reeves Patent Filters, manufactured by Messrs. Mather and Platt, Limited, of Salford, is another example of the class of self-cleansing filters.

Fig. 81 is an illustration of Roeckners Patent Clarifier.

The cylinders C dip below the surface of the water to be purified, which is contained in the reservoir A. They are open at their lower ends, but are closed at the top by the domes D. These are connected with the pump I by means of the pipes H. On starting the pump the water rises slowly in the cylinders. As soon as it reaches the level of the top, the action of the pump is stopped and the cocks K opened, when the water commences to flow down the pipes G, which together with the cylinders form a kind of syphon. If the reservoir A be kept full, the syphons can be made to act continuously. The flow of water being slow, insoluble impurities have time to subside.

The impurities may from time to time be removed by means of the small pump L connected with the bottom of the reservoir.

The clarifier can also be used for the purification of the effluent water from paper-mills.

The soluble impurities of water consist mainly of carbonate and sulphate of calcium and magnesia, together with traces of iron and organic matter. It is a moot point among paper-makers whether or not the presence of the two former in a water is objectionable. For boiling and bleaching purposes it undoubtedly is, as when mixed with caustic soda or bleaching liquor they form precipitates which line the insides of boilers, breakers, and potchers as a hard scale, which is always liable to become detached, and to find its way into the finished paper. Moreover, carbonates of calcium and magnesia are precipitated in the fibre, and carry with them a certain quantity of colouring matter, the subsequent removal of which is difficult.

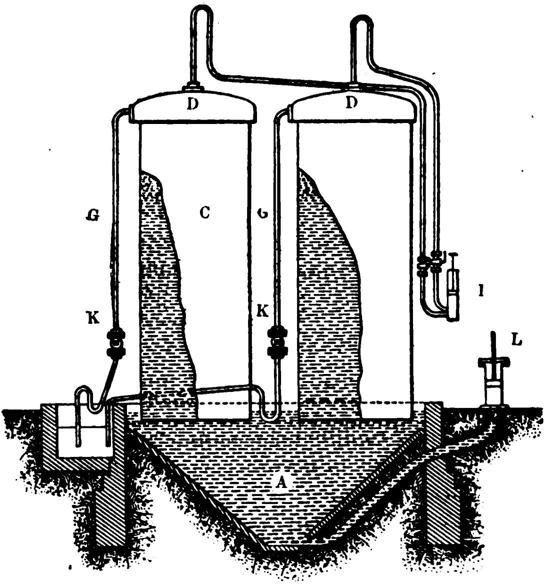

FIG. 81.

Carbonate of calcium, though practically insoluble in pure water, is soluble in water containing carbonic acid. When this carbonic acid is neutralised by lime or soda, the carbonate is precipitated. The sulphate of calcium is unacted upon by lime, but by the action of caustic soda is converted into free lime and sodium sulphate. The lime then neutralises the free carbonic acid in the water, and forms carbonate of calcium, which is of course precipitated.

These reactions may be represented by the following equations:—

$$1.\qquad \overbrace{\overset{\text{Calcium carbonate.}}{CaCO_3} + \overset{\text{Carbonic acid.}}{CO_2}}^{\text{Calcium bicarbonate.}} + \overset{\text{Lime.}}{CaO} = \overset{\text{Calcium carbonate.}}{2\,CaCO_3}.$$

$$2.\qquad \overset{\text{Calcium sulphate.}}{CaSO_4} + \overset{\text{Caustic soda,}}{2NaOH} = \overset{\text{Calcium hydrate.}}{CaH_2O_2} + \overset{\text{Sodium sulphate.}}{Na_2SO_4}$$

$$\overset{\text{Calcium hydrate.}}{CaH_2O_2} + \overset{\text{Carbonic acid.}}{CO_2} = \overset{\text{Calcium carbonate.}}{CaCO_3} + \overset{\text{Water.}}{H_2O}.$$

If sodium carbonate be used instead of caustic soda, the decomposition will take place thus:—

$$\overset{\text{Calcium sulphate.}}{CaSO_4} + \overset{\text{Sodium carbonate.}}{Na_2CO_3} = \overset{\text{Calcium carbonate.}}{CaCO_3} + \overset{\text{Sodium sulphate.}}{Na_2SO_4}.$$

It will be seen from the above equation that in the boiling processes the lime salts are removed from the water at the expense of an equivalent quantity of caustic soda. The same thing applies also to the salts of magnesia. The amount thus decomposed is not perhaps sufficiently large to make it advisable on that account to purify the water. It is indeed so small that processes of purification, based upon the use of lime and caustic soda, are now largely used, the cost for chemicals rarely exceeding 1*d.* per 1000 gallons. But for the reasons we have stated above, and also from the fact that it serves to remove dissolved iron and organic matter from a water, such a purification process is in certain cases advisable.

The processes now in use consist, as we have indicated, in the addition to the water of lime and caustic soda or carbonate of soda, the quantities being regulated according to the hardness of the water and the relative proportions of the carbonates and sulphates of calcium and magnesia.

The method of removing carbonates from water by the addition of lime is due to the late Dr. Clark, of Aberdeen, and the process is still called after him. It is in use in its original form in many places. The plant necessary consists simply of a tank for mixing the water and the lime, and of large settling tanks in which the carbonates of calcium and magnesia subside.

Various modifications of this process have been proposed, chiefly in the direction of improved plant.

In the Porter-Clark process the precipitate is removed by passing the water after the addition of lime (in the form of lime-water) through a filter-press.

In Fig. 82 is shown the Stanhope purifier, which is largely used for the purpose of softening water. The following details will render its action clear: A is a store tank containing caustic soda solution. B is a tank into which the water to be treated flows and which is maintained at a constant level by means of a valve and float. C and C are two tanks which are used alternately, and in which lime water is prepared. A definite quantity of caustic soda solution is added from B; this mixture forms the reagent by which the softening of the water is accomplished. D is a small tank for the purpose of maintaining a constant head of reagent. The reagent and the water are mixed together in the pipe F, the quantities being regulated by the cocks shown at H. The pipe F leads into the vessel E, which is fitted with a number of V-shaped shelves, placed at an angle of 45°, and riveted alternately to opposite sides of the vessel. This arrangement causes the water to take a serpentine course. The position of the shelves is indicated by the dotted lines.

As soon as the mixture of water and reagent flows down the pipe F, and enters the vessel E, the calcium and magnesium carbonates commence to precipitate and settle upon the V-shaped shelves. At the top of the tank a layer of wood shavings, inclosed in wire netting, is placed as shown by the dotted lines. This acts as a filter, and intercepts any particles that may not have subsided. The clear purified water passes away by the pipe I.

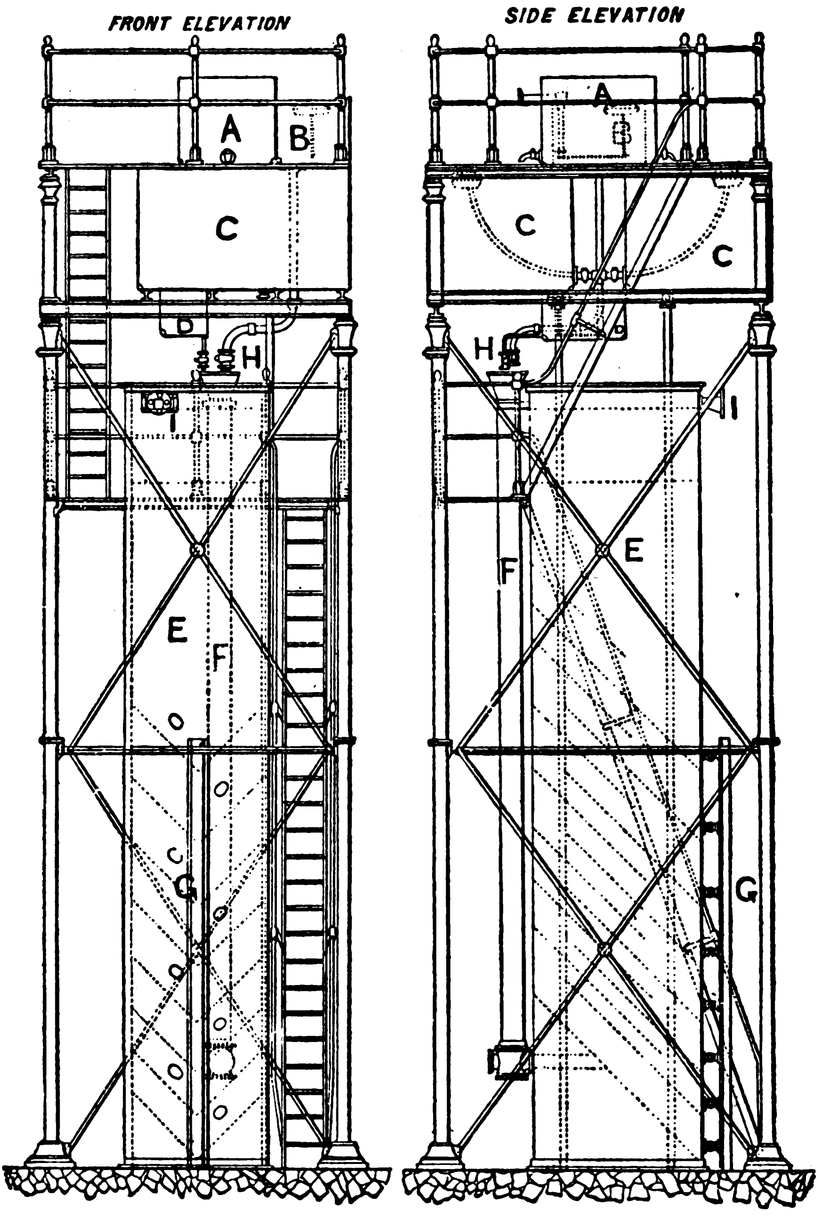

Fig. 82.

The precipitate that collects on the V-shaped plates is from time to time drawn off by the cocks shown at G; this may be done without interfering with the working of the apparatus. While there can be no doubt that the use of soft water is advantageous in the boiling, washing, and bleaching processes, and also of course for supplying steam boilers, it is probably an advantage to use a hard water for diluting the pulp before running it into the machine.

Continuous softening processes such as that just described are open to the serious objection that unequal results are frequently obtained owing to changes in the composition of the solution of chemicals or of the water itself.

Such an objection is obviated by the process of Messrs. Archbutt and Deeley, the plant for which is manufactured by Messrs. Mather and Platt, Ld. of Salford. The plant consists of two large tanks, one of which is being softened, while at the same time the other is being run off. The precipitate formed by the action of the lime and alkali used in softening is allowed to accumulate up to a certain point, and by the ingenious device of blowing up the precipitate by means of a current of steam and air it has been found that the freshly formed precipitate is carried down with such rapidity that practically clear water can be drawn off in about half an hour. By this means considerable economy in tank space is effected. Each tank-full of water can be tested and the proper amount of chemicals adjusted so that uniformity in composition of the softened water results.

In the case of papers which are loaded with any of the forms of calcium sulphate (pearl-hardening, crystal-hardening, &c.) the use of very soft water is objectionable from the fact that a certain quantity of calcium sulphate is dissolved. This would not take place to the same extent with water which is already charged with sulphate and carbonate of calcium.

The removal of soluble iron from a water is effected by the softening processes described.

CHAPTER XV.

ACTION OF CUPRAMMONIUM ON CELLULOSE. PREPARATION OF WILLESDEN PAPER.

THE action of a solution of copper oxide in ammonia upon cellulose has been already referred to (see p. 10). Celluloses, and also certain lignocelluloses, when treated with such a solution, gradually gelatinise and finally dissolve. On evaporating the solution to dryness, a gummy amorphous mass is obtained, containing the cellulose intermixed with copper oxide.

If the cellulose be in excess, e.g. when the solution is evaporated on the surface of paper, calico, &c., merely dipped in the solution, the copper oxide is often not formed at all, but a green varnish-like mass of cellulose combined with copper oxide, which coats the surface of each filament, welding and cementing them together. This cement-like *cuprocellulose*, as it may be termed, being insoluble in water communicates water-resisting properties to the material so treated: moreover, the presence of copper renders the fabric less prone than before to be attacked by insects and mould, so that animal and vegetable life of a parasitic nature and fungoid growths are rarely, if ever, to be observed, even when the material is kept under conditions where boring worms, ants, rot and mould, would be likely to attack it.

As has been already indicated (p. 9), the solution of cuprammonium hydroxide is preferable to one containing cuprammonium salts; not only is the action on cellulose more energetic, but various other advantages are obtained.

Preparation of the Copper Solution.—The cuprammonium solution is prepared according to the patent of Dr. C. R. Alder Wright (No. 737, 1883).

A series of cast-iron towers, two to three feet in diameter and ten to twelve feet high, is so arranged that a current of air can be blown by a powerful engine successively through the whole series. The towers are then nearly filled with fragments of metallic copper (crumbled up sheet, cuttings, &c.), and solution of ammonia; the air-current being turned on, oxidation of the copper and solution of the oxide so produced are rapidly effected.

The ammonia solution employed is previously impregnated with a considerable quantity of copper by passing a stream of water over scrap copper in similar towers, a current of ammonia gas mixed with a suitable proportion of air being at the same time forced in. The liquor passing from one tower is used over again to supply a second instead of water, and so on through the series: finally the liquor is brought up to full copper strength in the series of towers described above.

The spent air issuing from the towers carries with it a notable quantity of ammonia; this is intercepted by means of an "exhaust" scrubber containing copper, and well supplied with water, whereby a comparatively weak solution of ammonia and copper is obtained, which can be used instead of water in the first series of towers.

In order to produce the maximum effect on the cellulose, the solution should contain from 100 to 150 lbs. of ammonia and from 20 to 25 lbs. of copper per 100 gallons.

By decomposing a cuprammonium solution by means of metallic zinc, a corresponding solution of zinc-ammonium hydroxide can be obtained. This solution is also capable of gelatinising cellulose, but not to the same extent as the copper solution. It may, however, be advantageously employed in certain cases in conjunction with a copper solution. Such a solution can be conveniently prepared by substituting brass for copper in the dissolving-towers. It is worthy of note that although, as we have seen, zinc has the power of replacing copper in a cuprammonium solution, iron is without any action, although it readily replaces copper in a solution of copper sulphate. This fact is of very great industrial importance, as it enables the manufacturer to employ vessels and machinery of iron.

The 'Willesden' goods may be divided into two classes. Goods of the first class, such as rope, cordage, netting, &c., are prepared by simply dipping the made-up materials in a bath of cuprammonium solution, using certain precautions as to the mode of immersion and its duration, and the strength of the solution. On subsequently drying the dipped fabrics, they are obtained coated and impregnated with cupro-cellulose, which thus not only forms a kind of varnish-like surface dressing, but furthur adds strength to the fibres by more or less intimately cementing them together.

Goods of the second class constitute a much more important group to which at present the Willesden Company more especially devotes its attention. These fabrics are essentially of three kinds, viz. Willesden Canvas, Willesden Scrim, and Willesden Paper. The two former of these classes are prepared in much the same way as the goods just described, saving that the fabric to be treated is usually unwound from one roller and rewound upon another, after passing through the bath and over a succession of drying cylinders.

Willesden Paper.—This may be divided into two departments, viz. (1) Willesden unwelded; (2) Willesden welded, the first class being prepared from a single web of paper by passing it through the bath, rolling and drying. Certain coarse varieties furnish a waterproof material excellently adapted for lining packages, &c. Finer qualities furnish envelopes and stationery, possessing the valuable property of not being affected by water. Letters written on such paper would remain perfectly legible, even after prolonged immersion. It may be interesting to point out here that the cuprammonium solution offers a very simple means of fastening envelopes in such a way as to be proof against any attempts at tampering. The method consists in using a (*a*) Imports of cotton and linen rags:

1880.	1881.	1882.
29,642 tons.	26,773 tons.	21,200 tons.
451,782*l.*	396,274*l.*	303,349*l.*

1883.	1884.	1885.]
28,543 tons.	36,233 tons.	35,470 tons.
401,322*l.*	487,866*l.*	466,928*l.*

(*b*) Esparto and other material:

1880.	1881.	1882.
228,580 tons.	238,043 tons.	251,594 tons.
1,642,903*l.*	1,626,800*l.*	1,784,078*l.*

1883.	1884.
288,549 tons.	260,544 tons.
1,943,732*l.*	1,638,564*l.*

But a portion of these imports was exported again, the figures being as follows:—

(*a*) Exports of rags and other paper-making material produced in the United Kingdom:

1880.	1881.	1882.
55,792 tons.	50,488 tons.	49,352 tons.
673,523*l.*	563,460*l.*	526,554*l.*

1883.	1884.
51,293 tons.	60,924 tons.
502,851*l.*	562,903*l.*

(*b*) Exports of ditto of foreign and colonial produce:

1880.	1881.	1882.
6,965 tons.	10,183 tons.	7,004 tons.
102,499*l.*	146,101*l.*	84,515*l.*

1883.	1884.
11,561 tons.	26,498 tons.
121,992*l.*	274,664*l.*

The relative proportions of raw material furnished by the various countries in 1884 (the latest available return) are shown in the subjoined tables:—

(*a*) Imports of linen and cotton rags in 1884:

From	Tons.	£
Germany	21,280	294,883
Holland	4,406	56,537
Belgium	2,867	34,713
Turkey	2,036	16,228
France	1,875	28,133
Russia	1,784	33,293
Channel Islands	282	3,972
Norway	261	3,377
Denmark	198	3,020
British South Africa	133	1,615
Australasia	113	2,245
Canary Islands	96	1,043
Spain	93	1,009
Argentine Republic	64	1,280
Other Countries	745	6,518
	36,233	487,866

(*b*) Imports of esparto and other fibres in 1884:

From	Tons.	£
Algeria	88,357	515,232
Spain	40,159	314,927
Tripoli	33,930	172,282
Tunis	20,526	117,374
Other countries	1,033	5,738
	184,005	1,125,553

(*c*) Imports of other materials, including rag and wood pulps, in 1884:

From	Tons.	£
Norway	47,923	276,204
Belgium	7,169	58,383
Holland	6,484	46,104
Sweden	5,178	48,523
Germany	3,732	36,582
France	2,128	14,667
Denmark	1,205	13,332
British India	1,046	7,735
Egypt	870	4,933
Other countries	804	6,544
	76,539	513,011

A considerable export of raw material for paper-making also takes place from British shores, the figures, embracing rags and other materials, for 1884 being as below:—

(*a*) Exports of home produced rags and other paper-making materials in 1884:

To	Tons.	£
United States	59,222	550,924
Holland	649	2,703
British America	390	4,255
Germany	262	1,673
Other countries	401	3,348
	60,924	562,903

(*b*) Exports of foreign produced ditto in 1884:

(i.) Linen and cotton rags.

To	Tons.	£
United States	14,191	167,801
Other countries	514	5,519
	14,705	173,320

(ii.) Esparto and other fibres.

To	Tons.	£
All countries	140	701

(iii.) Pulps and other materials.

To	Tons.	£
United States	11,290	97,620
Other countries	363	3,023
	11,653	100,643

Our imports of 'rags and other paper-making materials' from Norway increased from 23,483 tons, value 138,098*l.*, in 1880, to 48,199 tons, 279,679*l.*, in 1884, mainly owing to the development of the wood pulp industry. Later figures will probably show a similar increment. The same articles from Denmark grew from 359 tons, 3406*l.*, in 1880, to 1403 tons, 16,352*l.*, from the same cause. German statistics have even a stronger upward tendency: 11,587 tons, 196,051*l.*, in 1880, against 196,051 tons, 331,591*l.*, in 1884. Our receipts of esparto from Algeria show an advance, but not a marked one, being 60,612 tons, 421,343*l.*, in 1880, and 88,357 tons, 515,232*l.*, in 1884. But shipments of the same fibre from Spain show a decline from 51,413 tons, 454,713*l.*, in 1880, to 40,159 tons, 314,927*l.*, in 1884; and from Morocco they have fallen away from 2879 tons, 18,231*l.*, in 1880, to 260 tons, 1290*l.*, in 1884; while the figures relating to Tunis and Tripoli also show a disposition to recede, though not at such a rapid rate.

The wood pulp industry of Norway for the year 1886 shows a very large increase upon the figures of a few years back, albeit prices have ruled very low. This latter circumstance is attributed, not so much to over-production, as to excessive competition among the sellers of this article. The quantity exported during the year 1886 is about 120,000 tons; in the year 1885 it was 107,651 tons; 1884, 88,220 tons; 1883, 70,464 tons; 1882, 58,884 tons; 1881, 42,194 tons; 1880, 26,055 tons. Several of the old works have extended their production during the past year, and several new establishments are in the course of erection, so the production this year may probably be put at 150,000 tons; wood pulp with 50 p.ct. water. The greatest part of the Norwegian wood pulp is exported to England, France and Belgium; in Russia, the increase in the duty has stopped business, and the same can almost be said of Germany. America, too, has drawn part of her supply from Norway, but this trade is not expected to continue.

The imports of raw materials during the last decade are given in the following official returns of the Board of Trade: "An Account of the Registered Quantities and Values of each kind of Paper-making Materials imported into the United Kingdom during each year from 1887 to 1898 inclusive."

Years.	Linen and Cotton Rags.		Esparto and other Vegetable Fibres.		Pulp of Wood.		Other Materials and Pulp of Rags.	
	Quantity.	Value.	Quantity.	Value.	Quantity.	Value.	Quantity.	Value.
	tons	£	tons	£	tons	£	tons	£
1887	38,273	466,167	200,116	962,049	79,533	511,367	60,120	332,669
1888	41,459	471,566	248,836	1,270,324	110,369	681,173	68,947	367,290
1889	42,443	426,322	217,256	1,090,266	122,179	690,692	46,282	306,537
1890	34,889	354,306	217,028	1,045,722	137,837	766,841	48,398	295,186
1891	32,824	317,555	212,666	1,033,938	156,609	851,389	37,099	258,668
1892	23,032	214,065	212,967	1,029,901	190,946	981,025	26,367	216,314
1893	20,758	199,155	185,450	870,431	215,920	1,184,265	30,358	231,119
1894	20,931	192,314	184,960	819,265	279,765	1,432,400	31,662	265,118
1895	25,033	229,645	186,408	791,236	297,095	1,574,302	25,058	181,713
1896	21,055	206,772	187,278	796,683	327,080	1,684,647	24,106	149,634
1897	25,333	249,631	204,579	825,195	388,304	1,939,761	20,326	135,653
1898*	20,859	193,803	197,341	768,779	404,827	1,894,328	..	..

The most striking features of these figures are: (1) the large relative increase of wood pulp, with corresponding increase in value; (2) the comparatively steady trade in esparto and rags, accompanied, however, by a falling off in values, which in the case of rags is conspicuously large.

Since the wood pulps rank as "half-stuff," it is clear that the main tendency of the paper manufacture of the United Kingdom is to increase in the direction of working up such half-stuff, and abandoning the chemical treatment of raw materials.

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* In this year the Board of Trade initiated a classified return of wood pulps, and the gross amount as given in the table was made up of *mechanical pulp*, 225,317 tons (value 668,302*l.*), and *chemical pulps*, 1,791,510 tons (value 1,226,026*l.*). Of the former, about 60 per cent. is imported from Scandinavia; of chemical pulps, the Scandinavian countries contribute about one-half.

Paper Trade of the United Kingdom.

The following classification of production will be of interest. It represents the results of very careful computation from statistics for the year 1895:

Brown	20
Grey (wrappings)	23
Printings (news)	16
„ (fine)	21
Writing	20
	100

It is interesting to note that these five main classes of papers are produced in approximately equal tonnage.

Manufactured Material.

Our import trade in manufactured paper has been growing of late years, as the following figures will show:—

Imports of paper and pasteboard, of all kinds except hangings:

1880.	1881.	1882.
1,021,952 cwt.	1,065,912 cwt.	1,098,118 cwt.
1,159,646*l.*	1,138,943*l.*	1,202,905*l.*

1883.	1884.
1,160,104 cwt.	1,447,335 cwt.
1,245,861*l.*	1,403,446*l.*

At the same time, our exports of manufactured paper, though amounting to only about one-third the weight, have very nearly as high an aggregate value as the imports, and have increased in much the same proportion in corresponding years. Thus:—

Exports of paper of all kinds but hangings:

1880.	1881.	1882.
472,168 cwt.	555,219 cwt.	584,947 cwt.
1,106,996*l.*	1,242,962*l.*	1,305,025*l.*

1883.	1884.
597,923 cwt.	670,760 cwt.
1,284,862*l.*	1,374,392*l.*

The above figures relate to paper manufactured in the United Kingdom. In addition, there were re-exports of paper of foreign and colonial manufacture to the following amounts :—

Re-exports of foreign-made paper:

1880.	1881.	1882.
68,843 cwt.	68,861 cwt.	50,403 cwt.
108,426*l*.	101,197*l*.	82,464*l*.

1883.	1884.
49,526 cwt.	51,467 cwt.
76,620*l*.	78,785*l*.

Taking the latest year for which detailed statistics are available, viz. 1884, we find that the importations of paper are derived from foreign states in the following proportions :—

Imports of paper in 1884—

(*a*) Writing or printing paper:

From	Cwt.	£
Germany	92,681	129,112
Belgium	42,139	68,370
Sweden	27,747	36,682
Holland	26,507	34,884
France	6,463	28,925
Austria	5,399	9,314
Norway	4,300	4,771
Other countries	3,174	5,655
	208,410	317,713

(*b*) Unenumerated sorts:

From	Cwt.	£
Germany	139,156	209,916
Sweden	116,488	120,793
Belgium	82,263	124,476
Holland	54,594	84,699
Norway	32,294	26,765
France	19,328	69,763
United States	10,980	31,201
Austria	5,927	12,012
Spain..	736	4,059
Japan	421	4,736
Other countries	3,547	5,995
	465,734	694,415

(*c*) Pasteboard and millboard:

From	Cwt.	£
Holland	439,749	201,894
Germany	235,658	116,185
Belgium	51,235	25,350
Sweden	32,331	20,241
Norway	8,260	5,726
France	3,262	19,259
Other countries	2,696	2,663
	773,191	391,318

The exports of home-made paper in the same year were distributed as follows:—

Exports of home-made paper in 1884—

(*a*) Writing, printing and envelopes:

To	Cwt.	£
Australasia	280,024	545,830
France	44,427	101,833
Bengal and Burma	33,963	71,834
Bombay and Scinde	29,767	64,227
British South Africa	16,900	33,041
British North America	14,871	44,511
Madras	10,532	25,651
Argentine Republic	8,683	30,954
United States	6,985	31,722
Sweden and Norway	6,101	11,870
Belgium	5,981	13,926
Germany	5,969	14,188
British West Indies	4,706	13,411
Ceylon	4,608	10,919
Other countries	31,397	93,454
	504,973	1,107,371

(*b*) Pasteboard and millboard:

To	Cwt.	£
Australasia	14,542	20,771
Bengal and Burma	5,147	4,589
Bombay and Scinde	4,572	4,134
France	987	2,309
Other countries	5,571	13,367
	30,819	45,170

(*c*) Unenumerated, and articles made as paper:

To	Cwt.	£
Australasia	62,731	81,385
British South Africa	9,341	11,809
Bombay and Scinde	7,146	10,389
Argentine Republic	6,283	8,113
Germany	5,147	11,394
Belgium	5,122	11,300
France	5,052	16,238
Bengal and Burma	5,006	6,678
United States	4,841	14,668
British America	3,737	7,801
Holland	2,410	5,529
Other countries	18,152	36,547
	134,968	221,851

The re-exports of foreign and colonial-made papers during the same period went to the following destinations:—

Re-exports of foreign paper in 1884—

(*a*) Printing and writing:

To	Cwt.	£
British India	10,488	14,643
Australasia	4,908	7,695
Other countries	3,236	7,554
	18,632	29,892

(*b*) Unenumerated:

To	Cwt.	£
British India	5,852	7,354
Egypt	5,167	7,751
Australasia	2,131	4,398
Russia	1,560	7,829
Other countries	8,465	15,825
	23,175	43,157

(*c*) Pasteboard and millboard:

To	Cwt.	£
All countries	9,660	5,736

(2) *Special.*—Classified returns of the working of a paper mill and its several departments, are just as necessary for the full control of the manufacture as are the 'account books' with the periodical balance sheet, for the proper working of the 'business' of the mill. Such returns fall obviously under the main heads of raw materials, labour, chemicals and steam. The further subdivision of the returns will take into account the various sections or departments of the mill; thus, the 'boiling' or half-stuff plant; bleaching, beating and machines, will be separately dealt with. In an esparto mill there will be special returns for the soda recovery plant, and in a sulphite mill for the liquor-making plant. The returns for boilers and steam raising will be controlled by periodical tests of evaporation in the boilers, and the combustion of coal in the furnaces by analysis of the flue gases.

The purpose of these returns is obviously to secure 'efficiency and economy' in all departments of the mill, to indicate all sources of waste or 'leakage,' and what is of course very important, to provide a statement of cost of every kind and quality of paper turned out. Such considerations are generally recognised and need not be further insisted on. There is, however, an aspect of statistical returns which is too often lost sight of, and that is that they provide permanent records of manufacturing experience. Such records have a practical usefulness in two directions, they provide against bad work, and for progressive improvement based upon continual observation of effects.

In regard to the planning and carrying out of an adequate system of statistics and records, only general instructions can be given. From the point of view of the ***business***, the one purpose is to arrive at costs per pound or per ton; from that of the ***manufacture*** the purpose is to give an account of every pound of material taken into work, in terms of final manufactured products, and as regards quality to refer the various items of quality of papers to the conditions obtaining in their production.

The latter order of statistics are those with which we are mainly concerned: they are the more comprehensive and include such returns from which actual money costs are calculated. We venture to think that the careful study of the preceding chapters of this work will supply the main outlines of a scheme of returns required, in any particular case. The knowledge which we have endeavoured to convey is based upon quantities and measurements; and that knowledge in practice implies the continued quantitative study of all the processes of the mill, as well as of the raw materials and finished papers. To take as an example the treatment of esparto: the following quantitative observations may be made.

Yield of half stuff—including yield of fibre from boilers after washing, and from potchers or press-pate after bleaching; proportion of caustic used in boiling; amount of dilution in boilers by condensation of steam; proportion of soda recovered; proportion of bleaching liquor used in potchers, and the amount of residual bleaching 'chlorine.' At the beaters, every item of the 'furnish' is carefully controlled, together with the agents used in antichloring, sizing and colouring; on the machine, in addition to a return of its turn-off in finished paper, observations are made upon the back water to determine fibre, loading, sizing and colouring constituents passing away unfixed by the wet web of paper: lastly the physical constants of the finished paper, which, in connection with records of all the previous treatments, gives a complete history of all that makes for quality.

It is unnecessary to prosecute this subject into minute detail. We repeat in conclusion that the paper-maker is only a 'technologist' in his art when his experience issues in the practice of precise records, and his control of a mill is based upon these essential statistics of production.

CHAPTER XVII.

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* Gives a list of works on Cellulose and its derivatives.

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