CHEMISTRY OF PULP
AND PAPER MAKING

CHEMISTRY OF PULP AND PAPER MAKING

BY

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THIRD EDITION

PREFACE TO THIRD EDITION

The objectives outlined in the preface to the first edition of this book have changed but little in the last twenty years, but conditions in the industry have changed with ever-increasing rapidity, and the technical literature of pulp and paper making has become very complicated and voluminous. This has made it much more difficult to bring the book up to date without increasing its size too greatly; the problem has really been to decide what could be omitted without too much loss, rather than to find suitable material to use. This has resulted in the decision to minimize or omit the more common methods of analysis, the details of which can be found easily in other places, but to include those which are more specialized or less easily found.

The book will perhaps be considered less positive and definite than former editions. Facts which were thought to be well established by the older investigations have had to be discarded or revised in the light of modern theories and knowledge. "Unlearning" such facts is fully as difficult as establishing them in the first place, but is often made necessary by finding that amounts of impurities or materials which were formerly considered without influence are actually important factors in the process. Further work along such lines will doubtless throw light on many former mysteries.

The first two editions of this book were entirely the work of one individual, but because of the facts just noted it was felt that no one person could do justice to all the subjects which it was desired to include. For this reason it was thought best to obtain the assistance of a number of collaborators, each of whom was an acknowledged authority in his particular line. Though multiple authorship has doubtless interfered to some extent with the continuity of style, this is a minor fault when compared with the greater breadth and value which it has been possible to give the book.

Grateful acknowledgment is made to the numerous individuals and firms who have supplied bits of information here and there, or allowed the use of illustrations, and also to the following contributing authors, without whose whole-hearted cooperation the work could not have been completed.

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PREFACE TO FIRST EDITION

The preparation of this book was undertaken because it was felt that there was need of a work dealing primarily with the chemical aspects of the pulp and paper industry and embodying under one cover the results of recent investigations along this line. The endeavor has been to include all details which the chemist should have to enable him to grasp the methods of manufacture, but it is not intended to be a treatise on paper making in all its mechanical phases, and in fact the mechanical features of the industry are discussed only in so far as they are necessary for a satisfactory understanding of the chemistry involved. It has been written chiefly with the idea of helping the young technical man, whether chemist or chemical engineer, and it has therefore been assumed that the reader has a fair knowledge of the elements of chemistry. At the same time it has been attempted to write as simply and plainly as possible and it is believed that any one connected with the pulp and paper industry will find it helpful and suggestive.

The subject matter has been collected from personal notes and experiences during the author's twenty years' service as chemist in the industry, as well as from a careful review of the literature relating to the subject. The latter is often contradictory in the extreme and in certain cases it has proved almost impossible to reconcile conflicting statements. In such cases both sides of the argument have been presented as fairly as possible. It is peculiar to the industry that there is usually a large number of variable factors which influence any one operation, and since it is practically impossible to control all of these variables it necessarily follows that results in different mills will not be in harmony. For this reason it is expected that the observant reader will find statements to which he will take exceptions, but such differences of opinion are often desirable since they indicate lines of investigation which will lead to a better understanding of many things which are at present obscure.

Regarding the methods of analysis and testing which are given it may be said that the attempt has been made to include all which are necessary for routine work in controlling operations. There are many occasional analyses which it is necessary to make during special investigations, but it is impracticable to include all of these; for such methods reference must be made to the numerous standard textbooks of analytical procedure.

Acknowledgment is made of the assistance of Mr. J. L. Merrill on the subject of " Straw " and also of that of my associates at the mills of S. D. Warren Company, whose encouragement has helped to overcome many difficulties.

I am also indebted to the publishers of Van Nostrand's Chemical Annual for a number of the tables which will be found in the appendix.

CONTENTS

CHAPTER I

CHAPTER II

CHAPTER III

CHAPTER IV

CHAPTER V

CHAPTER VI

CHAPTER VII

CHAPTER VIII

CHAPTER IX

CHAPTER X

CHAPTER XI

CHAPTER XII

CHAPTER XIII

CHAPTER XIV

CHAPTER XV

Sheet Making. Tests Applied. Bleach Requirement — Hypochlorite, Permanganate, Chlorine Consumption. Loss in Weight on Bleaching. Dirt. Chemical Properties — Alpha-Cellulose, Copper Number, Solubility in Caustic Soda, Ash, Viscosity, Lignin, Pitch. Tests for Chemical Pulps. Interpretation of Pulp Tests. *References.*

CHAPTER XVI

Sampling. *Microscopic Testing:* Fiber Composition. Spot Stains. *Specks and Spots.* *Physical Testing:* Conditioning Samples, Machine Direction, Wire or Felt Side, Basis Weight, Thickness, Expansion and Contraction, Opacity, Gloss, Color, Permeability, Smoothness, Picking. Strength Tests: Tensile, Bursting, Folding, Tearing, Flexural, Stiffness. Dirt. *Chemical Testing:* Moisture, Ash, Sizing Materials — Rosin, Starch, Glue, Casein; Alpha-Cellulose, Amount of Coating, Paraffin, Acidity, Sulfur and Silver Staining. *References.*

CHAPTER XVII

General. Letterpress or Relief Printing. Half-Tones. Planography. Intaglio. Printing Inks: Metallic, Heat-Set, Cold-Set, Water-Color. Paper from a Printing Standpoint: Formation, Uniformity, Specifications. Mechanical Imperfections in Paper: Wrinkles, Splices, Torn Sheets. Misregister. Picking. Complaints and Defects: Fuzz and Dirt, Poor Drying Ink, Offsetting, Lumps, Scumming, Strike Through, Grayness, Mottling, Smudging. Experiments in Printing. Rating Half-Tone Prints. Varnishing. *References.*

CHAPTER XVIII

General. Pulp Making. Beating. Practical Aspects: Formation, Pressing, Drying, Calendering. Moisture in Paper. Moisture *vs.* Printing. Waterproofing. *References.*

CHEMISTRY OF
PULP AND PAPER MAKING

CHAPTER I

CELLULOSE

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The Institute of Paper Chemistry

THE OCCURRENCE AND SEPARATION OF CELLULOSE

Occurrence and Forms. The century that has elapsed since Anselme Payen in 1838 discovered the common and preponderant component of all vegetable tissues and fibers, the material known as cellulose, has still left many gaps in the knowledge of this, the most abundant and important organic material on the face of the earth. Its increasing significance in industrial operations has resulted in an enormous amount of research, the results of which are extremely difficult to comprehend in their entirety. The presentation of the historical development and the detailed procedures will be left for other, more extended treatments, and this chapter will be devoted to a discussion of the present concept of cellulose and its properties, particularly as they affect the manufacture of pulp and paper.

Though the forms in which cellulose occurs are so varied that researchers formerly doubted that it was a true chemical substance, it has been shown that all plant tissues contain a material having the empirical formula $C_6H_{10}O_5$. This material is a carbohydrate which can be hydrolyzed to yield nearly the theoretical amount of glucose and is therefore regarded as being made up of anhydroglucose units. Various methods for the isolation of cellulose from the plant tissue depend on the action of alkalies, acids, oxidizing agents, and solvents to remove the impurities and leave behind the substance designated as cellulose. By these methods it is found that cellulose makes up (a) about 90 per

1

cent of seed fibers, such as cotton, kapok, and other flosses; (b) about 80 per cent of bast fibers, such as flax, ramie, and hemp; (c) about 60 per cent of wood fibers, such as spruce and pine; and (d) about 35 per cent of straw. The preparation of a standard cellulose to be used as the basis for fundamental studies was undertaken by the Cellulose Division of the American Chemical Society. The method recommended involves the treatment of cotton with solutions of alkali-rosin, alkali, and sodium hypochlorite, with many washings.[11]

As for so many colloidal natural materials, characterization is difficult, the methods of study are of necessity empirical, and the figures just given depend largely on the samples and on the methods used for their determination, since it is difficult to be sure that reactions designed to remove impurities may not also modify and solubilize portions of the cellulose itself. The impurities were formerly associated with cellulose as a basis of classification, as (a) the the lignocelluloses (where lignin occurs with cellulose in the bast fibers, cereal straws, and in wood); (b) the pecto- and mucocelluloses, such as flax, ramie, hemp, and the algae, fruits and tubers which contain materials related to pectic acid; and (c) the adipo- and cutocelluloses containing fatty and waxy materials such as those found in cork.[28] Such a classification is now largely of interest as indicating the types of accompanying materials with which the particular cellulose is associated.

In addition to cellulose, the cellular materials of many plants contain related carbohydrates called " hemicelluloses," which are differentiated by their insolubility in boiling water, their solubility in dilute aqueous alkalies, and their conversion into pentoses and hexoses on warming with dilute acids.

The sources, treatments, and uses of the commercially important forms of cellulose are given in Fig. 1 from Rue.[33]

The Microstructure of Cotton and Wood. Since cotton and wood constitute the greatest sources of cellulose, their structures are of significance in a consideration of the treatments employed in its isolation. The individual cotton hair consists of a long single tubular cell with one end attached to the seed. It is roughly cylindrical with a lumen or central canal containing protoplasm running through it. On ripening, the cell collapses and produces a flat, ribbonlike structure, twisted into an irregular spiral with 150–300 twists per inch. The lumen is surrounded by the secondary wall of cellulose layered in daily growth rings. Recently Anderson and Kerr[1] grew cotton under continuous illumination and at constant temperature, producing fibers free from these concentric layers in the secondary wall. Their photomicrographs of cross sections of the normal and of this special cotton are

shown in Fig. 2. Outside of the thick secondary wall is the primary wall or cuticle of spiral fibrils. In swelling agents, such as cuprammonium solution, the hair appears as a distended tube tied at intervals like a string of beads, where the strings of less readily swollen cuticle spirals constrict the swollen secondary wall structure in balloons.

In wood cells there is a somewhat similar structure, if one first takes into account the fact that the individual wood cells are not separate but

TEXTILE WASTE AND USED RAGS — WOOD — RAW COTTON — FLAX STRAW

COTTON SEED — Ginning — Retting

Mechanical and Chemical Purification NaOH, Na_2CO_3, CaO, Cl_2

Soda Digestion Na_2CO_3, CaO — Sulfate Digestion Na_2SO_4, S, CaO — Sulfite Digestion $CaCO_3$, S

Mechanical

SODA PULP — SULFATE PULP — SULFITE PULP

LINTERS & HULL FIBER — BALED COTTON — BAST FIBER

Chemical Purification and Bleaching NaOH, Cl_2, CaO

Chemical Purification and Bleaching Cl_2, NaOH, CaO

BLEACHED SODA PULP — BLEACHED SULFATE PULP — BLEACHED SULFITE PULP

Mechanical and Chemical Purification NaOH H_2SO_4 Cl_2 CaO

Spinning & Weaving

Further Purification NaOH, Cl_2 Acid etc

PURIFIED WOOD CELLULOSE — PURIFIED COTTON CELLULOSE

Paper Making

Solution and Regeneration
Xanthate Process NaOH, CS_2 — Cuprammonium Process Cu, NH_3 — Nitrate Process H_2SO_4, HNO_3

Esterification or Etherification
Acetylation Acetic Acid & Anhydride — Nitration H_2SO_4 HNO_3 — Etherification

TEXTILES

Chemical Fiber PAPER

Filament and Staple Rayon Began in U.S. in 1911
Transparent Wrappings Cellophane Sausage Casings Bottle Caps Began in U S in 1924

Filaments Glanzstoff

Filaments Discontinued in U S in 1934

Filaments Began in U S in 1919
Films Photographic Safety Glass
Lacquers
Plastics
Transparent Wrappings Kodapak Protectoid

Pyroxylin
Films Photographic Safety Glass
Lacquers
Plastics
Artificial Leather
Explosives Gun Cotton Gun Powder Dynamite
Cements

Filaments
Films
Lacquers

FIG. 1. SOME RELATIONSHIPS IN THE FAMILY OF CELLULOSE INDUSTRIES.

are bound together by non-cellulosic material filling the spaces between the cells. This non-crystalline (isotropic) material in the so-called middle lamella is chiefly lignin, together with some polymeric non-cellulosic carbohydrates. It confers rigidity and strength and acts as a cementing material for the wood structure. In contact with this middle-lamella material is the primary wall of the cell. It is anisotropic, that is, it gives some evidence of crystalline structure, and is composed of cellulose, together with some hemicellulosic material. Inside this thin primary wall is the bulky secondary wall, intensely

anisotropic and conspicuously laminated. This is made up chiefly of cellulose with some hemicellulose and lignin.

The laminated structure of the secondary wall contains from four or five to many concentric layers of cellulose, in which the cellulose units have a slight spiral orientation with respect to the fiber axis. The primary wall appears to be made up of transversely wound tight spirals, which, when wood fibers are swollen in cuprammonium, behave some-

A   B
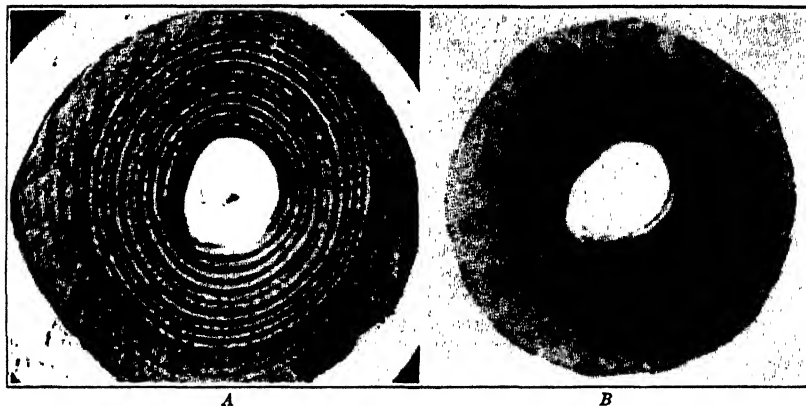
Anderson and Kerr.

FIG. 2. CROSS SECTIONS OF COTTON FIBERS.

A. Growth rings in swollen cross section of field-grown fiber. *B.* Swollen cross section of fiber grown under continuous illumination and uniform temperature conditions.

what as the cotton cuticle layer does. The secondary wall, which may be lined with a thin tertiary wall, surrounds the lumen.

The lignin and associated polysaccharides beneath the primary wall and between the layers of the secondary wall are there as an amorphous mixture having the appearance of a membrane. Lüdtke pictures a similar membrane separating each layer and even the smallest units of cellulose within the layer.

Figure 3 is a schematic representation of a cross section through wood fibers with the various structural elements indicated. This figure appeared with numerous actual photographs in an article by I. W. Bailey.[2]

The Fine Structure of Cellulose Fibers. The intensive investigation of the structure of cellulose as it exists in the plant and as it is isolated and subjected to various chemical treatments has brought rich results. X-ray studies have led to the picture of cellulose as a distinctly crystalline material made up of unit cells; these cells contain anhydroglucose chains and have the dimensions $a = 8.35 \text{ Å}$, $b = 10.3 \text{ Å}$, and

$c = 7.9$ Å. This length, 10.3 Å, in the direction of the fiber axis is twice the length of the single glucose residue and thus provides for the presence of cellobiose in the acetylosis products of cellulose. There is no evidence that this unit cell is in any respect a molecule of cellulose; it is merely the unit structure which must be repeated indefinitely to produce the observed x-ray diagrams. Figure 4 shows the unit crystal cell of cellulose from Meyer and Mark as given by Clark.[8]

In this chapter the following units and magnitudes will be referred to:

10 Å (Ångström units) = 1 millimicron (mμ) = 0.001 micron (μ) = 0.000001 mm. The practical limit of ordinary microscopic resolution is about 0.5 μ = 0.005 mm. The wavelength of the yellow sodium light D is nearly 5900 Å = 0.59 μ = 0.00059 mm. Most true molecules are less than 10 Å = 1 mμ in diameter, while the limits of the colloidal range have been proposed as 1 to 100 mμ.

a. Truly isotropic inter-cellular substance
b. Primary wall
c. Outer layer of secondary wall
d. Central layer of secondary wall
e. Inner layer of secondary wall

FIG. 3. SCHEMATIC CROSS SECTION OF WOOD CELLS. (Bailey.)

A. Transverse section of one entire fiber and of parts of seven others; B. section of adjacent walls more highly magnified.

These chains of glucose residues are bound together in the lengthwise direction through primary valences of oxygen atoms and appear to be bound together in the cross direction by " secondary valence " forces which may be effective between adjacent hydroxyl groups. The result of these forces is the formation of cellulose crystallite about 500 Å long by 50 Å in diameter. These crystallites tend to remain somewhat as units and to be associated with each other. In the development of the young cotton fiber Sisson[36] reported that crystalline cellulose may be noted in the x-ray picture as early as the fifth day when those impurities which obscure the x-ray picture are first removed. The improvement in the degree of orientation during the growth process of the natural hair has been demonstrated.

The microscopic investigation of the cellulose structure has shown

several aggregates. By mild solvent or swelling treatment Ritter[81] found in wood fibers threads called fibrils, arranged in sleevelike layers, 0.1 to 1 μ thick. In the inner layers the fibrils are spirally wrapped at angles of 10° to 30° to the fiber axis, whereas the outer layer contains fibrils wrapped almost at right angles to the fiber axis. He has
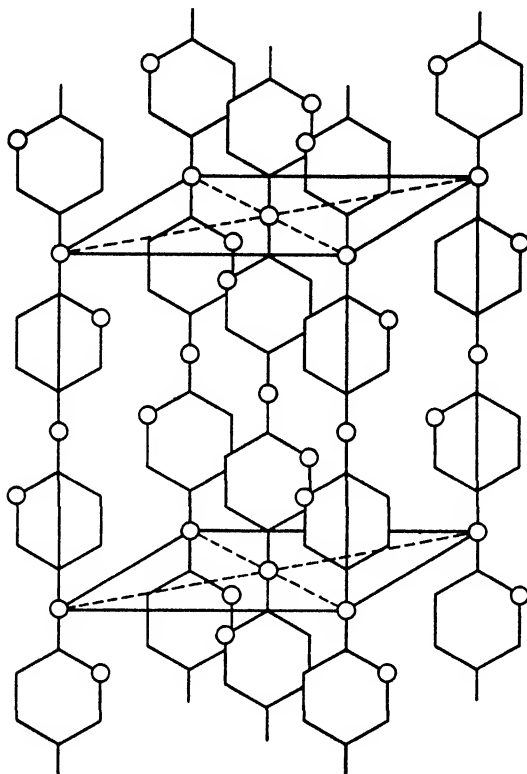
FIG. 4.   X-RAY UNIT CELL OF CELLULOSE.   (Meyer and Mark.)

isolated fibrils and fibril bundles as long as 230 μ. These fibrils in turn are made up of spindle-shaped units termed fusiform bodies and of still smaller spherical units (which may have resulted from swelling). All the units except the spherical ones show their crystalline nature by double refraction. Wiesner in 1884 described dustlike particles which he called "dermatosomes," while Mrs. Farr[12] and her collaborators have recently made extensive studies of ellipsoidal particles from cotton fibrils. The confusion of raw materials and methods has prevented reconciliation of these and other views in regard to unit structures.

Non-Cellulosic Components in Cotton and Wood. The natural impurities in raw cotton consist chiefly of pectic matter, coloring matter, oil, wax, albuminous matter, and inorganic salts. In a typical American cotton[28, page 29] the cellulose makes up 91 per cent of the total. The pectin compounds (0.53 per cent) are decomposed and removed by boiling alkali solutions. Oils and waxes (0.35 per cent) serve as a protective layer; they resist wetting and may be removed by solvents or more commonly by alkali. Protoplasmic residues account for the nitrogenous matter (0.2 per cent) and are removed along with the coloring matter during the usual alkaline treatments and bleaching. The ash content (0.12 per cent) may reflect the fertilizer conditions of culture and has been used to distinguish cotton types. The processes of purification, therefore, are aimed at the removal of nitrogenous matter and fat, the reduction of the ash content, and the preservation of the cellulose in an unchanged state.

Lignin. In wood the non-cellulosic components are much more plentiful and also more difficult to separate. The chief of these is lignin, and the processes of cooking and bleaching are designed to remove this component.

Lignin is a complex material generally characterized by the method used in isolating it from wood and by a series of color reactions. About 2 to 3 per cent of the lignin in sprucewood has recently been isolated by Brauns,[6] who employed solvents such as dioxane and alcohols in the absence of acids and bases. This fraction of the total lignin has been found to be structurally similar to the remainder of the lignin in the wood which requires for its isolation by dioxane or alcohol the addition of a small amount of acid. Native lignin has four methoxyl groups, four hydroxyl groups, and one carbonyl group for each unit of molecular weight of 840.

Lignin isolated from wood by the conventional methods differs from native lignin in that it is insoluble both in organic solvents and in sulfite cooking liquor. The native and isolated lignin give characteristic colors with phenols and aromatic amines and characteristic derivatives with phenol and thioglycolic acids. The methods used for isolating the total lignin fraction of the wood include the Willstätter method employing 42 per cent hydrochloric acid, the Klason method with 72 per cent sulfuric acid, and the Freudenberg method whereby the carbohydrates are dissolved in cuprammonium solution. Lignin may also be isolated as the sulfonic acid from sulfite waste liquor and as alkali lignin from the black liquor of the alkaline processes. These industrial lignins differ both from native lignin and the isolated lignin in that the lignin unit has been modified chemically during the pulping process.

Although much confusion exists regarding the structure of lignin and the condition of lignin in wood, there appears to be evidence in support of the idea that it is a polymeric substance built up of relatively simple units — native lignin would represent a low-molecular-weight polymer and the isolated lignin the higher forms. The formula shown in Fig. 5 represents one of the ideas put forth by Freudenberg[13] as to the structure of the lignin unit. This formula agrees in a general way with the molecular weight and number of methoxyl groups found by Brauns for native lignin. It also explains the formation of the cyclohexane derivatives isolated after pressure hydrogenation and of veratric acid and similar acids resulting from oxidation. The carbonyl group indicates how the hydrazone and diacetal are formed. This formula, however, does not show the phenolic hydroxyl group indicated for lignin. It is apparent that some work is still required before the chemist will know with certainty the chemical composition of the material being removed from wood in the pulping process.

The properties of lignin which enter into cooking and bleaching are not at all understood because of the uncertainty regarding its chemical structure. Sulfite cooking liquor at elevated temperatures reacts with lignin to form lignosulfonic acid; the calcium salts of this acid are precipitated when the waste liquor is treated with lime, and these are the basis for the processes leading to the manufacture of vanillin, tanning substitutes, etc. Alkaline cooking liquors form the so-called alkali-lignins which are soluble in the caustic solution. The sulfide in kraft liquor enters into reaction with lignin to form alkali-soluble sulfur-containing acids. Nitric acid forms a "nitrolignin" which is soluble in alcohol.

FIG. 5. STRUCTURAL FORMULA OF LIGNIN. (Freudenberg.)

Chlorine reacts with lignin to form chlorolignins which are soluble in alkaline solutions. A portion at least of the chlorine reacts by substitution, with the attendant formation of hydrochloric acid. Chlorine and hypochlorous acid will also oxidize lignin to alkali-soluble bodies. In the bleaching operation, chlorine and the hypochlorites react with residual lignin in the pulp; this lignin has been so modified by cooking

that the bleach reaction can no longer be considered as a reaction with wood lignin but rather with the insoluble products from the cooking step.

It seems probable that wood contains both free lignin and lignin combined with some carbohydrate material. The free lignin in the wood is very probably related to the native lignin described above; the combined lignin is related to the lignin requiring acid or alkali for its liberation.

According to Bixler,[5] soda and kraft liquors first remove the intercellular lignin rapidly and then attack the cell-wall lignin. The removal of the middle-lamella lignin by alkaline cooking produces fibers largely freed from this inelastic covering but still containing 7 to 8 per cent lignin and producing paper of high physical strength. Continued cooking removes lignin of the secondary wall and also affects the carbohydrates, so that the softened fibers exhibit diminished strength. In contrast with this, sulfite liquors appear to penetrate the fiber lumen and to dissolve both cell-wall and middle-lamella lignin, while they also attack the carbohydrate components.

The Hemicelluloses. The second important non-cellulosic component of wood consists of a group of compounds called hemicelluloses. The substances covered by this term do not comprise a definite class of chemical compounds but rather they represent all the carbohydrates and carbohydrate derivatives in wood apart from cellulose. They include polymeric forms of the hexose sugars, mannose and galactose, known as mannans and galactans, and of the pentose sugars, xylose and arabinose, known as xylans and arabans; derivatives of these sugars, such as the methyl pentoses; and mixtures of the hexoses and pentoses, such as glucoxylan. The hemicelluloses of some woods, notably the western larch, contain large quantities of a mixed arabano-galactan. In addition to the polymeric forms of these simple sugars, there may be present and grouped together as hemicelluloses the oxidation products of sugars such as the uronic acids. Certain of the gums which are classed as hemicelluloses are mixed compounds of sugar and a uronic acid. Thus it will be seen that no clear-cut definition is possible for a hemicellulose. The term is rather a group term indicating the non-cellulose carbohydrates present in wood, although at times it is defined as the material soluble in either dilute acid or dilute alkaline solutions.

Minor Components of Wood. In addition to cellulose, lignin, and hemicelluloses, wood contains also smaller amounts of resins, terpenes, fats, nitrogenous matter, tannin, coloring matter, and mineral ash. Typical analyses are given in Table 1 for a characteristic softwood, jack pine, and for a characteristic hardwood, birch. These figures will

vary widely for samples taken at different locations within the tree and from different trees.

TABLE 1

CHEMICAL COMPOSITION OF TYPICAL WOODS*

	Jack Pine	Birch
	%	%
Lignin	28.4	22.1
Pentosans[1]	10.7	21.2
Cellulose[2]	52.2	44.9
Mannan	5.5	0.2
Methoxyl[3]	1.7	1.4
Acetyl	1.5	3.2
Uronic acid[4]	3.6	4.8
Ash	0.3	0.4

1. Pentosans — less 3/2 CO_2.
2. Cellulose — Cross and Bevan cellulose less pentosans and ash.
3. Methoxyl — analysis less lignin × 17.5 (22.5 for hardwoods).
4. Uronic acid — CO_2 × 4.

REDUCING SUGARS RESULTING FROM THE ACID HYDROLYSIS OF WOOD
(Different wood samples from those described above)

Total reducing sugar	68.7	70.8
Glucose	46.4	47.9
Mannose	9.7	1.3
Galactose	4.3	0.0
Xylose	6.1	21.3
Arabinose	2.2	0.3

* Analytical values selected from the files of the Institute of Paper Chemistry; individual sugar values determined by selective fermentation with the exception of mannose which was estimated as phenylhydrazone.

In the above analyses of wood, the jack pine totals somewhat more than 100 per cent because of the presence of mannan in the Cross and Bevan cellulose.

In the quantitative examination of cellulose-containing materials, several methods are designed to remove the lignin components. Ritter and his associates prepared "holocellulose," which contained all the carbohydrates, including the hemicelluloses freed from lignin, by treatment with chlorine gas followed by alcoholic solutions of organic bases. In the estimation of cellulose, the most popular method is that of Cross and Bevan which depends on chlorination and extraction by sodium sulfite solutions, removing lignin and some hemicelluloses. Other meth-

ods employed include that of Norman and Jenkins (using sodium hypochlorite) and that of Kürschner and Hoffer (using alcoholic nitric acid).[30]   The above methods are empirical, depend on close adherence to specified procedures, and give values which differ somewhat from each other.   Each product so prepared is designated by the method, such as Cross and Bevan cellulose.*   None of them are specific for polyanhydroglucose (chemically pure cellulose) in pulps, although the value is probably approached in extracted cotton.

The cellulose isolated by such methods may be further tested by treatment in 17 to 18 per cent sodium hydroxide solutions.   The portion of cellulose undissolved by this reagent under carefully outlined conditions is designated alpha (α)-cellulose, the portion dissolved and capable of being reprecipitated by acids is called beta (β)-cellulose, and the dissolved portion which does not precipitate is gamma (γ)-cellulose.

Lignin is generally estimated by hydrolyzing the carbohydrate to water-soluble products, using either 72 per cent sulfuric acid or 42 per cent hydrochloric acid for the purpose.

THE MOLECULAR STRUCTURE OF CELLULOSE

Organic Structure.   The form and structure of cellulose having been discussed briefly, the next step is a study of the still finer structure of these particles and fibers.   In the historical development, the attack of the organic chemists has established the following facts.   The purer the form of cellulose, the more closely its empirical composition agrees with that for $C_6H_{10}O_5$.   (A high-grade muslin rag stock shows 44.31 per cent carbon and 6.18 per cent hydrogen; $C_6H_{10}O_5$ will yield 44.44 per cent carbon and 6.17 per cent hydrogen.)   Methylation of cellulose gives a product containing 44.6 per cent methoxyl compared with a theoretical 45.6 per cent for three methoxyl groups for each $C_6H_{10}O_5$ unit.   The product of hydrolysis and methylation of cotton is identical with 2,3,6-trimethylglucose.   This can be obtained in 86 per cent yield.

Acetylation of cellulose results in the formation of a triacetate containing three acetate groups for each glucose unit.   Combined acetylation and hydrolysis (acetolysis) of cotton forms the octa-acetate of a disaccharide known as cellobiose, which consists of two glucose residues united by a 1,4-beta-glucosidic linkage and normally results in about

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* Analytical methods for the determination of alpha-, beta-, and gamma-cellulose as well as of Cross and Bevan cellulose and pentosans are included in the " Standard Methods " of the Technical Association of the Pulp and Paper Industry.   The modified Forest Products Laboratory method for lignin determination is described by Ritter, Seborg, and Mitchell.[32]

40 per cent yield from cotton. Since the acetic acid-sulfuric acid treatment destroys about half the cellobiose produced, the conclusion can be drawn that cellulose is composed of cellobiose to the extent of at least 60 per cent. Cellotriose and cellotetrose have also been identified among the products of hydrochloric acid hydrolysis of wood.

β-— Glucopyranose.   α — Glucopyranose.   Aldose form of Glucose.

Cellobiose.

Cellobiose group.   Cellobiose group.

Linkage between two cellobiose groups as found in the cellulose chain.
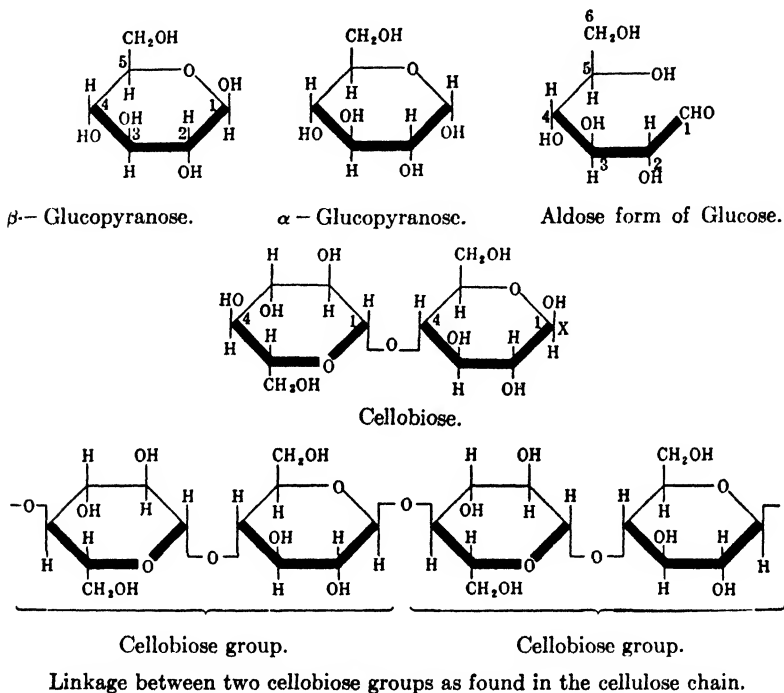
FIG. 6. STRUCTURAL FORMULAS. (Haworth.)

It is generally accepted that the cellulose molecule consists of a long chain of glucose units linked by 1,4-glucosidic oxygen bonds as shown in the well-known Haworth[16] formula (Fig. 6).

Each glucose residue contains three free hydroxyl groups to account for the trimethyl and triacetate derivatives. The terminal glucose group, having four hydroxyl groups, should form on hydrolysis and complete methylation a tetramethylglucose, and Haworth reports the isolation of this substance.

Colloidal Structure. The properties of cellulose and its derivatives are properties of colloidal systems, and the elucidation of the colloidal structures of the gels and sols of cellulose is still a live subject of investigation. Cellulose is a polymeric substance whose molecule (macro-

molecule) is built up of closely similar repeating units (glucose). The problem may be expressed as the discovery of how many glucose residues are united in the single chain and how many chains cling together under the various chemical and physical changes. To call these surviving aggregates molecules appears to be a matter of definition. Certainly they do appear to be held together by powerful forces and to survive nitration, acetylation, etc., relatively unchanged in magnitude.[25] It is wholly probable that the same cellulose could be treated in such a way as to have units half or one-tenth as large, which would still survive the same reactions. What, then, is the molecular weight of cellulose? One might as well ask how long is a string of beads or how long is an anchor chain? Obviously the answer depends on their history, and it is impossible to say when, on cutting, they cease to become strings of beads or anchor chains.

This question for cellulose does not appear capable of a final answer with the evidence now available, if indeed it has any answer. Conceivably the degradation of the chains will give aggregates which show many of the specific properties which we now ascribe to cellulose. The investigation of the so-called molecular weight of cellulose is not merely an academic hobby, for it has immediate and very useful applications. The degree of polymerization (the number of glucose units in the average particle) is closely related to the physical and, to a lesser extent, the chemical properties of polymeric substances. Carefully purified native cotton is composed of cellulose aggregates having a much higher average degree of polymerization than a purified wood pulp, and the latter will show a wide spread in degree of polymerization for its aggregates. Highly polymeric cellulose, in general, yields stronger viscose, paper, or other products, and the determination of the degree of polymerization at various stages of a process reveals where the depolymerization (degradation) is taking place and its magnitude, although it is recognized that other factors than the degree of polymerization are related to the strength factor.

Among the methods for the determination of the degree of polymerization, by far the most widely used is the one involving the determination of the viscosity. By the study of simpler substances it has been shown that viscosity is directly related to the molecular weight of the dissolved molecules, and Staudinger and others have applied this to cellulose and its derivatives, especially in cuprammonium solutions.

For certain highly polymeric hydrocarbons the particle weights can be determined by freezing-point depressions, and they agree fairly well with the viscosities calculated. Such substances exhibit particle weights

up to 10,000 and are designated hemicolloids because their magnitude is intermediate between true crystalline compounds and the colloids. Much larger than the hemicolloids are the high-molecular " molecular colloids," " macromolecules," or eucolloids which show particle weights up to 200,000 to 300,000, exhibit abnormally high specific viscosities, and possess the properties of such natural products as rubber and cellulose.

The abnormally high viscosity of cellulose in cuprammonium hydroxide or of cellulose derivatives in various solvents is explained on the basis that it is not a question of simple chain arrangements of the atoms, but one of six-membered rings. From the observed viscosities, Staudinger (1934) calculated the degree of polymerization for some common materials as ramie 1000, cotton 750, sulfite pulp 230–310, cellulose acetate 150–250, and regenerated cellulose 100–250. Since each glucose residue in the chain contributes 162 atomic-weight units, the " molecular weight " for cellulose will be 162 times the degree of polymerization or about 120,000 for this sample of cotton cellulose. The purest form of cotton shows degree of polymerization values ranging up to 2000–2600; raw cotton linters may start at 1400 and finish at 200–400 in finished rayon by any of the four common processes. The lower the value the greater will be the ease of dispersion, and the lower will be such physical properties of rayons as breaking strength, bending strength, and extensibility. This also applies to paper, especially for the general strength characteristics such as fold endurance, although it should be emphasized that a straight-line relation does not exist. A recent paper[39] from Staudinger's laboratory reports that alpha-celluloses have an average polymerization degree of 150 and higher, beta-celluloses of 10–150, and that gamma-celluloses fall below 10.

The second method for the determination of particle size is that involving the use of the ultracentrifuge for sedimentation velocity or equilibrium measurements. These measurements gave Stamm particle weights of the order of 40,000, whereas Kraemer has reported values from 100,000 to 300,000 for cotton-linter alpha-cellulose.

While cellulose will not disperse in suitable solvents, certain cellulose derivatives have been examined by means of colligative properties such as freezing point and osmotic pressure. Freezing point has been abandoned as completely untrustworthy, but osmotic-pressure measurements are still offered in comparison with or contrast to the values obtained by other methods. A tabulation[28] in Marsh and Wood, page 357, shows degree of polymerization values calculated from osmotic measurements for cellulose nitrate ranging from 25 to 1600, for cellulose acetate from 80 to 380.

On the assumption that each glucose chain ends in a reducing (alde-hyde) group and that all reducing power is resident in this terminal group, calculations have been made by the copper number, by the iodine number, or by the yield of tetramethylglucose, etc., which indi-cate that the degree of polymerization for native celluloses is of the order of 50–175.   This is the end-group method.

These varied methods for the determination of the degree of polymeri-zation yield values from 10 to 2000–3000 or give particle weights from 1500 to 500,000.   This can only emphasize the wide diversity in the samples included under the general term " cellulose," and the lack of agreement among the various methods.   Indeed, not one of the methods employed is without serious and fundamental criticism, and it appears wholly inadvisable to accept the results of any of them as giving a basic constant for a chemical substance.

Methods of Swelling and Dispersing Cellulose.   In native cellulose the glucose chains occur bound into crystallite bundles which may be dispersed (" dissolved ") in certain concentrated aqueous solutions. It is probable that the process of dispersion always involves some deg-radation and that the cellulose regenerated by precipitation from such solvents is altered to give either a " hydrate cellulose " with an ex-panded crystal lattice and increased sorptive power or a " hydro-oxycellulose " without change in the x-ray picture but with a superficial hydrolysis or oxidation.   Whether or not the dispersed particles (micelles) in solution are ever identical with the crystallites of the original fiber is open to question; certainly they are so large that the systems cannot be designated true solutions but do behave as colloidal dispersions.

When wood fibers are placed in the dispersing agents, there is first penetration of the solvent through the outer wall into the cellulose layers.   Processes of adsorption, imbibition, or actual combination produce a swelling of the fiber by a mechanism somewhat resembling osmotic flow, until the swelling pressure causes a rupture in the outer primary wall.   It is at this stage that these less readily swollen, trans-versely wound outer wall portions act as strings to constrict the swelling of the secondary wall which protrudes between them in balloons. Finally, an effective swelling agent produces some of the microscopic particles mentioned above, and these disperse to submicroscopic parti-cles.   Dilution of such sols with water or treatment with suitable chemicals precipitates the cellulose.   Thus are illustrated the colloidal phenomena of sorption, swelling, dispersion, and coagulation.

Among the dispersing agents for cellulose, the ammoniacal solution of copper hydroxide is by far the most important.   A typical cupram-

monium solution contains 15 grams copper, 200 grams ammonia, and
1 gram sucrose per liter. Approximately 5 per cent dispersions of native
cellulose or 10 per cent dispersions of oxidized cellulose can be prepared.
The mechanism of this dispersion as well as of the others remains
obscure. Some investigators believe in a compound formation, others
in adsorption of the copper complex. The solvent power increases with
the concentration of the copper, with the alkalinity (to a maximum),
and with previous degradation of the cellulose by alkalies, acids, oxi-
dizing agents, heat, etc. The viscosity of a 1 per cent dispersion under
specified conditions of temperature and concentration of copper and
ammonium hydroxide has been standardized by the Technical Associa-
tion of the Pulp and Paper Industry for use in indicating the quality
of pulps. Cellulose regenerated from cuprammonium solution is in
the " hydrate " state.

The action of alkalies on cellulose has been extensively studied since
Mercer in 1850 took out the patent on the process bearing his name
involving a treatment of cotton with cold concentrated sodium hy-
droxide. Solutions of this alkali at sufficiently low temperatures
($-10°$ C.) will disperse cellulose. The reaction is accelerated by addi-
tions of zinc hydroxide. Many other strong alkalies such as potassium
hydroxide, tetramethylammonium hydroxide, and similar compounds
are able to swell and disperse cellulose.

Concentrated acids such as sulfuric, hydrochloric, and phosphoric
acids act as solvents for cellulose but effect prompt and extensive
hydrolytic degradation. Hot concentrated salt dispersions of cellulose
have been produced, especially in such salts as zinc chloride, ferric
chloride, calcium, or lithium thiocyanates.

THE CHEMICAL PROPERTIES OF CELLULOSE

Reactivity. The evaluation of the structure of cellulose as made up
of chains of polyanhydroglucose residues grew out of and in turn
stimulated the study of the chemical behavior of cellulose reactions.
In general, cellulose is not highly reactive, and several of the purifica-
tion methods depend on its inertness toward reagents capable of remov-
ing impurities. The most reactive groups include the one primary
alcohol and the two secondary alcohol and the hydroxyl groups in the
glucose unit and the oxygen bridge between these units. In many cases
the changes are colloidal or topochemical and take place on the external
and internal surfaces of the aggregates. The magnitude of these effects
may be understood from Stamm's[37] estimate that the internal surface
of 1 gram of cellulose is between 1 and 10 million square centimeters.

Acids. The action of acids on cellulose results in a weakening of the product and yields at the same time a whole range of degradation products which may even include glucose when the hydrolysis is continued for a sufficiently long period or at elevated temperature. In general, the rate of hydrolysis is associated with the strength of the acid — the stronger the acid the more rapid the degradation. On the other hand, the action of cold concentrated sulfuric acid for a short period is to convert the cellulose fibers into a vegetable parchment by a localized action on the surface of the fibers. For longer periods or at higher temperatures a charring takes place. Dilute sulfuric acid forms the material designated as " hydrocellulose," exhibiting reduced strength properties and increased copper number, alkali solubility, and degradation of the chain lengths. Acids of the type of nitric acid behave in a somewhat different manner, for the concentrated acid, particularly in the presence of a dehydrating agent, forms nitrocellulose, whereas dilute nitric acid both oxidizes and hydrolyzes the cellulose to give a product termed " oxyhydrocellulose." Paralleling the chemical degradation of the cellulose is a physical change in fiber structure; where the hydrolysis is extensive, the fiber falls into a fine powder with considerably increased solubility in water and alkalies. The loss in strength of cellulose materials under the influence of acid hydrolysis is of great significance; for example, papers to be used for permanent records should contain or develop a minimum acidity. It appears that small amounts of basic fillers, such as calcium carbonate, are able to inhibit this deterioration on aging.[15]

Alkalies. It has been pointed out above that alkalies are able to swell cellulose at low concentrations and to produce dispersions at high concentrations. With a freshly regenerated viscose cellulose, alkali concentrations of 1.5 to 3.3 N gave clear sols which were flocculated by dilution or by higher alkali concentrations. The mass of data on the action of caustic soda on cellulose at room temperature is large and confusing. It appears that below 10 to 12 per cent sodium hydroxide little permanent change is produced, with 10 to 20 per cent sodium hydroxide a new x-ray picture appears, and above 20 per cent a new structure seems to form. Many chemists have yielded to the temptation to designate these as sodium cellulosates of various compositions, whereas others find no clear evidence of compound formation. Certainly the alkali opens up the fiber structure and leads to an enhanced reactivity when dilution results in desorption of the alkali and production of hydrate cellulose. In the presence of air, alkali leads to marked disintegration of cellulose. This may be observed when an improperly washed alpha-cellulose residue is being dried to constant weight at

105° C. The white material becomes brown and may even gain an appreciable amount in weight.

Oxidizing Agents. The action of oxidizing agents, as dichromates, ozone, permanganates, and hypochlorites, on cellulose produces an indefinite material known as "oxycellulose." Acid oxidation tends to produce a material with low capacity for absorption of methylene blue and a high copper number, whereas alkaline oxidation gives an oxycellulose with the opposite characteristics. The alkaline product possesses a more acidic nature as is shown by its enhanced solubility in alkalies, while the more strongly reducing type prepared in acid solutions gives reactions commonly associated with carbonyl groups. The detection and determination of oxycellulose depend on these reactions, as well as on specific colors, stain reactions, and affinity for other dyes. Oxidation processes usually effect a degradation of the cellulose, revealed by reduced viscosity values.

The Action of Light and Heat. Light appears to catalyze certain reactions of chemicals with cellulose. In peroxide bleaching of cotton goods Hirschkind and collaborators[19] found that ultraviolet light longer than 4000 Å had little effect, that light shorter than 3000 Å degraded cellulose, and that the most effective range was 3500 to 3850 Å. In general, the curves showing the loss in viscosity as cellulose is degraded by ultraviolet light are similar to those obtained when cellulose is degraded by dilute acids.[26]

Heat alone brings about destructive distillation of cellulose to such end products as ethylene, carbon monoxide, methyl alcohol, acetone, and acetic acid, as well as the final carbon dioxide and methane. With less drastic treatments, such as would be involved in artificial aging by heating pulps in a stream of air at 100° C., the strength characteristics such as tear and bursting strength are decreased, while the copper number and acidity are increased. The fold endurance is a most sensitive test for the apparent hydrolytic degradation occurring from heat, and papers made from acid-cooked furnishes are more susceptible to such loss than those from alkaline-cooked stocks.

Because of the practical implications, the combined action of heat and water is of great interest. There appears to be little action below about 150° C., but over the range 170 to 260° C. the cellulose decomposes to give gaseous and liquid products. Above 150° C. water is lost irreversibly, the copper number increases, and the viscosity falls, but such degradation is minimized in inert atmospheres. A mixture of air and steam will cause rapid disintegration of fibers at high pressures, although steam alone is without effect. Extensive hydrolysis produces glucose which at higher temperatures may be converted to oxymethyl-

turfural. Fiber structure is lost at 200° C., and at 250° C. the cellulosic material has become practically amorphous. The influence of oxygen on the nature of the product is considerable.

The Action of Microorganisms on Cellulose. It has been found that several species of bacteria are able to ferment cellulose. In aërobic fermentation, the reaction is mainly an oxidation with evolution of carbon dioxide; whereas in anaërobic, in the absence of oxygen, the reduction process produces methane. In both there is probably extensive hydrolysis as a first stage. A recent study[41] of the action of *Cytophaga Hutchinsoni* showed that two-thirds of the cellulose attacked appeared as carbon dioxide and one-third as a mucilaginous oxycellulose of the acidic non-reducing type. A 50 per cent decomposition of cellulose in eight days was reported. There is evidence[29] that lignin retards or inhibits such bacterial attack. These reactions are of direct significance in the problem of stream pollution by pulp and paper mill and other industrial wastes, in the disposal of domestic sewage, in the soil solution of cellulosic materials, and in many other processes.

Cellulose Derivatives — Esters. Although the manufacture of esters and ethers of cellulose may not seem to concern pulp and paper making directly, the rapidly increasing amounts of wood pulp used in place of cotton linters in the preparation of these derivatives warrants a thorough discussion of their properties and of the reactions involved in their preparation. In addition, there seems to be a very real application for certain of the materials as sizing agents and for the improvement of wet strength and other characteristics.

In point of historical development, the cellulose nitrates have priority and will be discussed first. The basic reaction is the replacement of the hydroxyl groups in the glucose residues by nitrate groups, and the formulas for the individual products with the corresponding nitrogen content are trinitrate $C_6H_7O_2(NO_3)_3$ — 14.2 per cent N; dinitrate $C_6H_8O_3(NO_3)_2$ — 11.1 per cent N; and mononitrate $C_6H_9O_4(NO_3)$ — 6.8 per cent N. The most highly nitrated cellulose, guncotton, is prepared by treating purified cotton waste with about 30 times its weight of a mixture of 75 per cent sulfuric acid, 15.75 per cent nitric acid, 1.3 per cent nitrous acid, and 7.95 per cent water at 15° C. This reaction proceeds without visible change in the physical structure of the cellulose fiber, and a product is obtained which is soluble in acetone or ethyl acetate but not in alcohol or ether-alcohol. Decreased nitric and sulfuric acid concentrations produce materials of lower nitrogen content, and in all cases the products appear to be mixtures of higher and lower nitrates. The product containing about 2.5 nitrate groups per glucose residue (12.8 per cent N) is known as collodion or pyroxylin and was

the first artificial silk or rayon as made by Chardonnet. It is soluble in acetone, ethyl or amyl acetate, methyl alcohol, and ether-alcohol mixtures.

The most significant physical characteristics of nitrocelluloses are solubility and viscosity. The solubility is primarily dependent upon the degree of nitration, but for the viscosities the conditions of preparation and the history of the cellulose are determinative. Both properties are dependent upon the degree of polymerization of the original cellulose and of the final product. Many of the uses depend on a suitable balance of these factors. The nitration grades are about as follows: guncottons (more than 13 per cent N); pyrocollodions (12.6 to 12.8 per cent N), soluble in alcohol-ether, ethyl acetate, etc., used in small-arms ammunition; pyroxylins (11.5 to 12 per cent N) in numerous grades of solubility, flow, adhesion, compatibility with oils, etc.; collodions (11.5 to 12.5 per cent N), soluble or gelatinizing in ethanol alone; and celluloids (10.6 to 10.9 per cent N) as thermoplastic pyroxylins of high viscosity and tensile strength. For rayon and other applications where the high inflammability of such products is not permissible, they may be denitrated by reducing agents, such as ammonium sulfide, to leave a regenerated cellulose. No rayon made from cellulose nitrate is now reported. Nitrocellulose solutions for emulsions of the pyroxylin grade find some use in the coating of paper for improving water and grease resistance, the prevention of moisture transmission, and appearance.

For rayon purposes a second ester is important. This is the acetate, produced by treating cellulose with a mixture of acetic anhydride, glacial acetic acid, and a catalyst such as zinc chloride or phosphoric, sulfuric, or chloroacetic acids. Subsequent steps in the usual operation include: (a) hydrolysis by careful addition of water and acetic acid; (b) ripening; (c) precipitation by addition of a large excess of water containing alkali for neutralization; and (d) washing, centrifuging, and drying the product. Although the triacetate is first prepared, the steps listed above are designed to hydrolyze some of the acetate groups, so that the final product contains between two and three such groups per glucose residue. Celanese and Lustron are rayons made by such processes. Many products of cellulose acetate have been developed, including yarns, fabrics, bristles, safety moving-picture film, films for preservation of documents, microfilms for records, lacquers, and plastics. Wide variations in the products available with acetyl contents between 36 to 42 per cent and with viscosities from 5 to 500 seconds permit ready adaptability. Mixed esters are likewise finding technical applications.

By far the most important form of rayon is that prepared by the viscose process. The nomenclature of these compounds, like that of

the nitrate, is questioned, for they are not strictly esters of xanthogenic acid $C = \begin{cases} OR \\ S \\ SH \end{cases}$ but esters of dithiocarboxylic acid $C = \begin{cases} OH \\ S \\ SH \end{cases}$ and the material prepared is sodium cellulose dithiocarbonate. Alkali cellulose is prepared in the first step by treating cotton linters or wood-pulp cellulose in a mercerizing bath of 17.5 per cent sodium hydroxide for 1 to 2 hours at 20° C. This dissolves the hemicelluloses, which are largely removed by pressing out the excess alkali. The resultant alkali cellulose is shredded and aged at 20° C. for 70 hours, when oxidation in open containers with free access of air shortens the chain length and lowers the viscosity correspondingly. The next stage is the xanthation when alkali cellulose reacts with carbon disulfide to produce cellulose xanthate.

$$C_6H_{10}O_5 - C_6H_9O_4 - ONa \ + \ CS_2 \ \longrightarrow \ C_6H_{10}O_5 - C_6H_9O_4 - O - \underset{\underset{S}{\parallel}}{C} - SNa$$
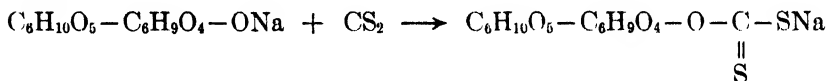
The xanthate occurs as a highly polymeric material which is partially hydrolyzed to regenerated cellulose in caustic soda solutions. On standing, the hydrolysis of the viscose solution "ripens" it, and colloidal changes take place which can be best followed by viscosity measurements. There is at first a rapid fall in viscosity (0 to 2 days), then a slow rise during the next 12 days, and finally a rapid rise after about 14 days. This rapid increase in viscosity leads to the development of gel structure which is remarkable for its property of syneresis, i.e., in contracting and squeezing out the immobilized water. In commercial practice this ripening process is interrupted at about 4 days, and the solution is spun.

In the preparation of rayon filaments the ripened secondary cellulose acetate may be dissolved in acetone and then forced through tiny orifices into coagulating baths of oils or salt solutions, or it may be spun by projecting the solution into a closed compartment where the solvent is evaporated by hot air. A similar dry process applies to the spinning of cellulose nitrate. For viscose rayon the alkaline viscose solution is forced into an acid coagulating bath to yield a regenerated cellulose containing 75 to 80 per cent alpha-cellulose plus degraded cellulose and non-cellulosic carbohydrates.

Cellulose Derivatives — Ethers. In recent years the commercial production of the cellulose ethers has attained some importance, and many have been prepared and studied experimentally. One of the earliest methods for making methylcelluloses was based on the reaction

between alkali cellulose and a 15 per cent solution of sodium hydroxide and dimethyl sulfate. An easier method involved the treatment of cellulose acetate in acetone solution with dimethyl sulfate and 30 per cent caustic added simultaneously.[17] With high degrees of substitution the products are soluble in organic solvents; many are plastic or thermoplastic, and they form water-resistant films. A lower stage of methylation (22 to 26 per cent methoxyl) gives materials soluble in water which are used in printing pastes because of their precipitation on warming. They are available commercially as Colloresin, Tylose, and Glutoline for use as emulsifying agents, binding agents, etc. The materials of the lowest methoxyl content require 5 to 12 per cent sodium hydroxide solution for their dispersion, which may be aided by cooling, and they have been suggested to replace viscose.

Ethylcellulose is produced in similar fashion, using ethyl chloride or ethyl sulfate. Again, lower ethers with ethoxy contents as low as 5 per cent are soluble in caustic solutions. The 27 per cent ethoxy product dissolves in water, whereas an ethoxy content raised to 47 per cent gives materials soluble in organic solvents. The normal commercial product has two hydroxyl groups replaced, although a triethylcellulose, like trimethylcellulose, can be obtained in crystalline condition.

Among the many other alkyl and aryl cellulose ethers, benzylcellulose deserves mention. It is offered commercially as the dibenzylcellulose which is soluble in a wide range of solvents and has industrial applications similar to those of cellulose acetate. It has low affinity for water and possesses other useful properties.

The early source of cellulose for the esters and ethers was cotton or cotton linters, but the economics of the situation long ago brought about the introduction of wood pulps. For the acetate process cotton linters have dominated the field due to the interference of the degradation products in even the best wood pulps. In the other processes mentioned, wood pulps containing above 92 per cent or cotton above 98 per cent alpha-cellulose are acceptable. Excellent results are reported from 40 to 60 mixtures of wood and cotton. The wood pulps used must possess sufficient strength to stand wet handling in sheets or rolls and must allow good penetration of the reagents. The alpha content mentioned above must be associated with a copper number not greater than 1.5, and a low ash, particularly in regard to calcium, copper, manganese, and iron. The allowable viscosity of suitable pulps may vary widely and will depend on the cooking process and the conditions. A high viscosity is neither required nor desired in pulps used for conversion so long as the alpha-cellulose and copper-number values are satisfactory.

THE COLLOIDAL PROPERTIES OF CELLULOSE

Gel Structure. Though it has been necessary to introduce colloidal reactions and properties throughout the early pages of this chapter, there are still certain additional specific colloidal characteristics which are of intimate concern in all the treatments and uses of cellulose. The excellent review of Stamm[37] will supply detailed information and references both as regards cellulose in general and wood in particular. The outstanding colloidal property of cellulose is its character as a gel with all that it implies. Cellulose in fibers, films, and other structures shows definite analogies to such gels as glue and agar, and the gain and loss of water is of tremendous significance.

In a pulp pad or a sheet of paper the gross units of the structure are fibers of cellulose and their composite fibrils. The fibers themselves, however, possess still a finer structure in terms of the aggregating of chains of anhydroglucose units into something like the native crystallites. Interspersed between the fibers and even possibly between the crystallites will be spaces generally filled with air and responsible for much of the opacity of the sheet as light is reflected or scattered. At points of contact such aggregates will be held together more or less rigidly, and the nature of the bonds will determine some of the physical characteristics of the sheet. With the films and fibers of regenerated cellulose produced from dispersions, the units will be smaller, and they will be oriented or not oriented in terms of the methods of preparation, such as speed of extrusion, tension, nature of coagulating bath, etc. Even in the natural fibers like cotton the x-ray investigation seems to show that there is a relationship between the degree of orientation of the crystallites and the tensile strength.

For an understanding of the structure of cellulose in the solid state, the recent work of Frey-Wyssling[14] and others is of especial interest. Although the x-ray data give no clue in regard to the empty spaces in the fiber, the existence of such spaces is necessary to explain the water swelling and the colloid dyestuff adsorption which takes place without alteration of the x-ray diagram. The possibility of esterification of all the hydroxyl groups without destruction of the fiber structure likewise indicates that all the chains are essentially exposed to the action of such reagents and not enclosed in a solid structure. By the precipitation of colloidal gold or silver these spaces have been filled, and measurement of these metal crystallites shows that the long vacant spaces are from 50 to 100 Å in diameter. This also demonstrates that the fiber structure consists of the long crystallites (about 60 Å broad) bound to each other by smaller bundles of the chains and surrounded by empty spaces.

It follows that such a material will show a characteristic capillary structure which will be demonstrated in various ways. This will apply to the pores in the fibers themselves as just discussed, as well as to the interfiber spaces. Measurement of the air pressure necessary to displace water or other liquids from the capillaries gave pore radii of 900 to 2500 Å for cellulose nitrate membranes, while the largest radii of pores in wood sections were still larger. Such measurements involve a number of uncertainties, and no generalization as to results can be drawn. Other methods employed include: permeability to gases and liquids; rates of diffusion of acids, alkalies, and many other substances; a combination of pressure-permeability and capillary cross-section measurements; ultrafiltration tests; rate of capillary rise of liquids in sheets; and estimation based on the moisture content and the relative vapor pressure. Applying this last method to wood cells, Stamm[37] reports a distribution of particle sizes of capillaries, with 6.5 Å $= 0.65$ mμ as the most probable and 50 Å as the average radius of pores in the cell walls themselves. This capillary structure has large significance in such reactions as acetylation, where the well-oriented ramie fibers present a more closely packed structure and show decreased rate of reaction than the less-oriented cotton with wider intermicellar spaces. Hydrogen-diffusion rates depend on orientation, and the expanded structures of cellulose derivatives as celluloid, nitrocellulose, and triacetylcellulose are reported[9] to show 200 to 300 times the permeability of regenerated cellulose.

The Cellulose-Water Relation. Of all the colloidal properties of cellulose, its adsorption of water is most important in the pulp and paper industry. That this is truly an adsorption of water vapor has been proved conclusively;[20] even up to 150° C. there is agreement with the Freundlich adsorption relation and no compound formation. At low humidities there is a good sorption of water until about 3 per cent moisture is taken up; over most of the range there is a slower increase in sorption,* until above 80 per cent humidity the water sorption rapidly increases and may approach 28 to 30 per cent, which is the fiber saturation point of the wood. These fiber saturation water contents decrease with temperature and depend on the materials. Typical values for wood pulps or isolated lignin range between 22 and 30 per cent, while bleached pulps, alpha-cellulose, or standard cotton may go as low as 15 per cent. Of the rayons, cuprammonium rayon may hold

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* Because it is often impossible to distinguish between adsorption (one substance is concentrated on the surface of another) and absorption (one substance intimately interpenetrates another), in this chapter the term *sorption* (verb, *sorb*), suggested by McBain, will be used to cover both phenomena.

35 to 41 per cent, viscose rayon 33 to 45 per cent, acetate rayons 18 per cent, and nitrocellulose 6.7 per cent water in equilibrium with saturated water vapor.

Cellulose samples taken to a high humidity and then subjected to atmospheres of lower humidity sorb more water at a given humidity
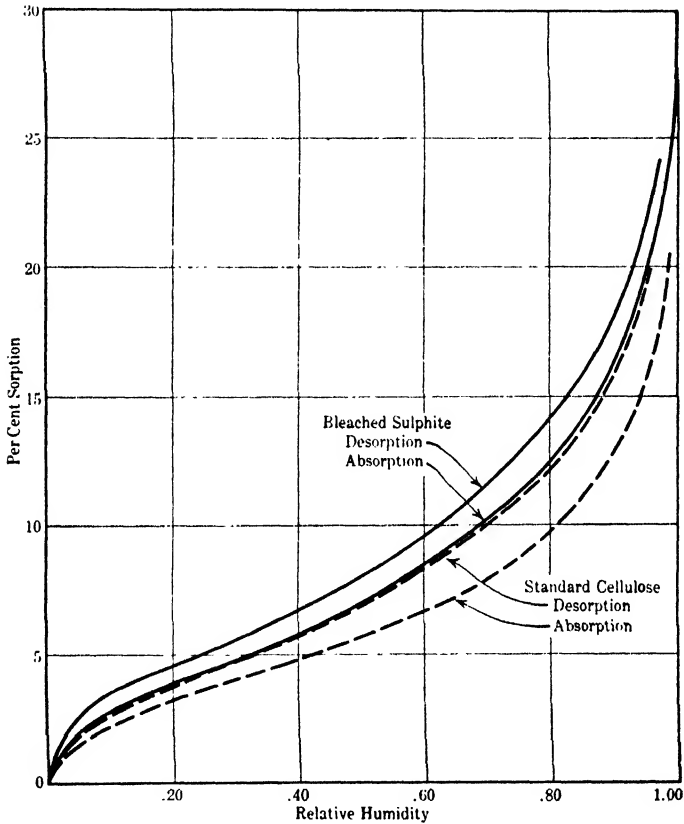
Fig. 7.   Sorption Isotherms: Water Vapor.

than these same samples which have been raised from low humidities to the humidity at which the determination is made.   This means that the sorption curve is not retraceable but the sorptions for the decreasing humidities are above those for the increasing humidities.   At the ends the curves coincide fairly well, and the loop between them is called the hysteresis loop.   Typical curves for standard cellulose and bleached sulfite pulp are shown in Fig. 7 from Maass and Campbell.[27]   The

most reasonable of many suggested explanations seems to be that sorption of water is chiefly on the secondary valences of the hydroxyl groups on the cellulose chains. In a water-soaked condition these free groups are practically satisfied by water, but as drying proceeds, some of the hydroxyl groups from adjacent chains mutually satisfy each other, and a part of them may not be freed for water sorption on the upward cycle, thus accounting for decreased effectiveness. This avidity for moisture is diminished by bleaching or preheating, while a thorough steaming or even soaking in water gives an enhanced water sorption capacity. Bleached sulfite pulps have a higher capacity than cotton cellulose. Oxycellulose and hydrocellulose are slightly less active sorbents than the cellulose from which they were made, while cellulose hydrate obtained by the action of 20 per cent caustic on cellulose, by regeneration from cuprammonium dispersions, or from cellulose acetate all give increased moisture sorption over the whole vapor-pressure range. Heat is given off when water vapor is sorbed, so that sorption is less at high temperatures.

The swelling resulting from the sorption of water vapor or liquid is of significance in countless paper and textile operations. Direct swelling and shrinking measurements have been made on individual spruce sulfite fibers by Weidner,[42] who reported that, on the first desorption from 95 to 0 per cent relative humidity, the length decreased 1.5 to 1.6 per cent while the diameter decreased 9.0 to 9.6 per cent. Subsequent cycles showed length changes of 0.8 per cent and width changes from 7.4 to 8.3 per cent. Stamm[37] has reported numerous studies on wood, showing the anisotropy of swelling with various sections. Such dimensional changes become of great moment in many printing processes where moisture changes between color runs produce misregister or where curling of sheets or boards makes handling difficult. Many similar studies have been made with paper and paper boards.

Swelling phenomena also are observed in water, and in many solutions. The process of beating pulp is a case in point. The evidence indicates that the word " hydration " in this connection is not accurate, for highly beaten pulps possess no greater hydration capacity than unbeaten pulps, if both are dried and subjected to the vapor sorption tests. It appears that the effect of beating is to produce an increase in the external surface at the expense of internal surface by crushing the fiber bundles and providing greater areas of contact for the fiber-fiber forces. Pentosans present in pulps or similar materials added to the beater increase the capacity of the pulp to develop its strength in the beater. If beating depends upon a mechanical disruption of the intercrystallite and interfibrillar bonds, the mechanism by which the

hysteresis loop was explained may throw light on the well-known irreversible strength loss in dried pulp.

In many aqueous solutions, however, cellulose shows wide degrees of swelling, and again the lyotropic series comes into play. Stamm gives the listing for the swelling effect on wood:

$$Zn > Li > Ca > Mg > Mn > Ba > Na > NH_4 > K$$
$$CNS > I > CrO_4 > Br > Cl > NO_3 > SO_4 > ClO_3$$
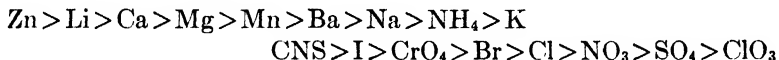
Cellulose swells appreciably in strong alkalies but not in dilute mineral acids. Kanamaru[21] reported that with Cellophane sheets minimum swelling occurs at pH 6.7 and 11.5, and maxima at pH 5.7 and 8.5. It is known commercially that changes in pH produce noticeable changes in the width of the sheet coming from a machine. The mechanism of these effects is obscure, but they may be associated with differences in the electrokinetic potential.

Of the many investigations of the cellulose-water relation, the work of Maass and Campbell[27] and their associates in Canada and of Stamm[37] at Madison has been extensive and informative. It appears that when bone-dry pulp is exposed to low pressures of water vapor a tremendous force of attraction is exerted. This causes sorption of about 3 per cent water which is held on the cellulose with an initial bonding force of cellulosic materials for water about twice the attraction between the molecules of water themselves.[38] It is stated that bone-dry cellulose will actually take water vapor away from the vapor sorbed on phosphorous pentoxide. This first water is sorbed with a high heat of sorption which drops rapidly from 250 calories per gram at 0 per cent to 50 calories per gram at 7 per cent water and then slowly falls to 0 at the fiber saturation point. It is estimated that this first water has a specific volume of 0.921 and that the effective force that would cause this compression is 2420 kg. per sq. cm. Such bound water does not freeze down to $-25°$ C. but is held in some immobile form.

Now, as the relative humidity increases, water continues to be sorbed, but less readily, and it appears that, after the first most active areas are covered, subsequent sorbed water fills the capillary spaces. Such capillary-held water would expose sharply curved menisci whose curvature would result in a decreased vapor-pressure equilibrium relation, and this is one of the methods for the calculation of the capillary sizes. With ordinary cotton and many pulps and sheets, usual room humidities give about 6 to 8 per cent moisture retained, although the moisture content of cellulose may be influenced by the pH, by the drying procedure, or by fillers. As a standard in the paper industry, it is a general

custom to consider that 100 pounds of air-dry pulp will yield 90 pounds of bone-dry fiber when dried at 100° C.

It is probable that there are continuous variations in the method and forces of sorption ranging continuously from the first strongly bound portion to the last water in large capillaries which is essentially free water. The evidence for any definite hydrates of cellulose is not convincing, although the various formulas suggested do possibly indicate the hydrophilic character of the various fiber surfaces. Some evidence is accumulating that the adsorbed water may be held in an oriented layer which reflects its dielectric constant and that displacement is possible only with more strongly polar solvents such as cellosolve (ethylene glycol monoethyl ether, $C_2H_5OCH_2CH_2OH$). Such oriented sorption of water affects the degree of fiber swelling and may play a role in the bulking of paper. Paper containing less than 5 per cent moisture is likely to show increasing static electricity on handling, and to minimize trouble from this cause printers are advised to keep the humidity at 50 per cent, or higher.

Other Sorptive Properties of Cellulose. In addition to water, cellulose and its derivatives are capable of sorbing many organic liquids and swelling in some of them. Several of the alcohols are sorbed and retained much as water is and show the same general type of hysteresis loop. Substances of lower polar character are less strongly sorbed and are more readily removed by heat and vacuum treatments. Prolonged drying at 105° C. fails to remove strongly sorbed alcohol, which is retained in amounts large enough (1.5 to 2 per cent) to interfere seriously with the accuracy of analytical methods.[43] The size of the fiber openings comes into consideration, since the larger molecules of higher alcohols may not penetrate into the spaces freely penetrated by water. In non-polar hydrocarbons and benzene, swelling is negligible, but in the alcohols or fatty acids, there is swelling which decreases as the molecular weight of the liquid increases. By first swelling in water, it is possible to replace this in turn by ether or acetone and then by a hydrocarbon or benzene without large change in the swollen dimensions. Kistler[23] applied this method, using propane as a final liquid which was then evaporated, leaving an aerogel of Cellophane with increased air content.

The sorption by cellulose of many materials from aqueous solutions is fundamental in many processes. Acids are only slightly adsorbed from dilute solutions, and the ash seems to be an important factor, sometimes functioning by an exchange adsorption mechanism. The work of Kanamaru in terms of swelling-pH studies has been mentioned; he has also reported that a sample of Cellophane sorbed hydrogen ions

preferentially below pH 7.4 and hydroxyl ions above this, but this " apparent isoelectric point " varies with the previous treatment of the Cellophane.

Cellulose-Alkali Systems. In the previous sections the action of alkalies on cellulose has been discussed without a full expression of the phenomena, which after 95 years remains one of the most highly controversial in the chemistry of cellulose. The x-ray evidence indicates that, as cellulose is exposed to increasing concentrations of sodium hydroxide, there is no change below about 10 per cent. With concentrations above 10 per cent there is a change in the pattern, and a gradual shift to a third pattern occurs with alkali concentrations above 20 per cent. Schramek[35] designates the 10 to 20 per cent form sodium-cellulose I and the high-concentration form sodium-cellulose II. On dilution of the reaction mixtures, desorption of the alkali or slow hydrolysis produces two additional products which finally change to a hydrate cellulose form.

The evidence from the changed x-ray diagram is not conclusive between the possibilities of (a) reaction of the alkali, with the cellulose considered as a very weak monobasic acid, and (b) the adsorption of alkali to produce the observed swelling and opening up of the whole structure of the crystallites. The numerous titration methods to demonstrate the extent of the alkali taken up by cellulose have also failed to give definite results because of the simultaneously enhanced water sorption by the solid and the difficulty of removing the water from the product. The criteria of compound formation by the phase-rule test would require such data as were reported by Kolthoff.[24] This work indicated that cellulose takes up sodium hydroxide in accordance with the partition law up to 8 per cent concentration. Between 8 and 24 per cent, the amount taken up increases greatly but is independent of the concentration, while at 32 per cent there is another decided increase in the amount taken up which is also independent of the concentration. Many attempts to establish such relations have produced a mass of data which some people interpret in terms of compound formation, and others as merely adsorption of the alkali on the cellulose. Bancroft and Calkin[3] favor the adsorption theory, with the further suggestion that, although no clear evidence of a stoichiometric sodium cellulosate exists, it still may be possible that small amounts of such material may be formed and may be adsorbed on essentially unchanged cellulose. It appears that such material is then able to react with carbon disulfide in the xanthation process and to peptize the rest of the cellulose. The products of xanthation always appear to be mixtures of higher, lower, and unchanged products. Recent extensive studies of the action

of alkalies on cellulose have shown that the order of their effectiveness in swelling follows the lyotropic series found in so many colloidal phenomena and that the amounts of alkali taken up furnish poor evidence to support the concept of compound formation.[34]

The sorption of salts on cellulose from dilute solutions is usually small and selective. From more concentrated solutions there is sometimes positive sorption as with NaCl, KCl, $CaCl_2$, and KCNS, and sometimes water is more strongly sorbed as from LiCl solutions. The sorption depends somewhat on the history and ash of the cellulose and upon the characteristics of the salts in question. Various observers have reported that cellulose selectively sorbs oxides of aluminum, chromium, iron, tin, and lead from solutions of their salts. This is a result of hydrolysis and is aided by temperature and increase in pH up to a limit. Bialkowsky[4] concluded that the ease of sizing of such pulps as kraft, groundwood, or unbleached sulfite is connected with their preferential sorption of alkali, whereby they are able to displace the hydrolysis equilibrium of sodium resinate and produce free rosin to precipitate on the fibers.

In the dyeing of cellulose many experiments have demonstrated the validity of the Freundlich adsorption isotherm relation. The data are abundant and generalizations difficult, but the colloidal point of view appears most fruitful. In the next section the electrokinetic charge on cellulose will be discussed more fully so that it will suffice here to say that in most aqueous systems cellulose particles are negatively charged. It follows that positive ions will be strongly sorbed as is true of the basic dyes, while acid dye negative ions will be poorly sorbed, and the generally weakly negative direct colors fall in between these. Various conditions such as pH, salt additions, and temperature are able to affect the degree of sorption of the dyes, and one view holds that good dyeing depends on particles tiny enough to penetrate the cellulose fibers. Certainly the entrance of the dye into the fiber is a diffusion process of varying speeds, but whether it is strongly held or not depends on surface forces of sorption. If cellulose is mordanted with aluminum hydroxide (as from alum), the charge becomes positive and acid dyes anions can be adsorbed. Similarly, materials of the wetting-agent type with complex positive or negative ions aid in the adsorption of acid or basic dyes, respectively. There seem to be three ways in which dyes are held: (a) by salt formation, (b) by solid solution of the dye in the fiber, or (c) particularly for direct dyes on cellulose, a special kind of crystallization (sorption) of the dye in and on the surface of the crystallites. The measure of dyestuff sorption has frequently indicated that various forms of cellulose and its derivatives

possess of the order of 10 million square centimeters of this internal surface per gram of solid. Active carbon gives comparable or somewhat lower values.

The Electrokinetic Properties of Cellulose. Any solid in contact with a liquid assumes an electric charge with respect to the liquid. If the solid is a small, negatively charged particle suspended in water, it will migrate toward a positively charged electrode (electrophoresis); if the solid is a porous wall, a capillary, or a series of capillary spaces as in a pulp pad which is kept motionless, the water will flow through it toward the negatively charged electrode (electroendosmose), and the rate of such movements is proportional to the charge (zeta or electrokinetic potential). As pointed out in the section on dye sorption, cellulose is normally negatively charged, either by the ionization of positive ions from surface groups or the sorption of negative ions (such as hydroxyl) on its surface, and this affects many of its adsorption characteristics. At high pH this charge is highest, and it decreases over the pH range down to 2, approaching zero. Addition of salts of the type of calcium chloride decreases the zeta potential with increase in concentration, aluminum salts are even more effective, and the tetravalent thorium is able to reduce the charge to zero at very low concentrations, and then slight salt additions give the cellulose a positive charge. Figure 8 shows data of Briggs[7] and demonstrates this effect of strongly sorbed polyvalent ions on surfaces of the opposite charge. In general, a large value for zeta potential is associated with high hydration of the surface. The significance of this has been pointed out by Kanamaru[22] in connection with swelling of fibers and the sheets made from them. Evidence is accumulating that the sign and magnitude of the charge on the cellulose fibers are of great significance in the sizing of pulp, its dyeing, its retention of fillers, starches, and fiber fines, and even the mutual flocculation of the fibers themselves which affects formation of the sheet. In general, the zeta potential on cellulose fibers in distilled water is of the order of 8 to 25 millivolts — values below those shown by many other colloidal materials.

THE PHYSICAL PROPERTIES OF CELLULOSE

Density. Since cellulose is utilized largely in the natural fiber condition or in regenerated cellulose from these fibers, the physical properties of the various samples of cellulose will be expected to vary somewhat. It has been shown that cellulose does not adsorb helium gas; a number of measurements have been made of its specific volume in helium. For a standard cellulose in helium, Maass and Campbell[27]
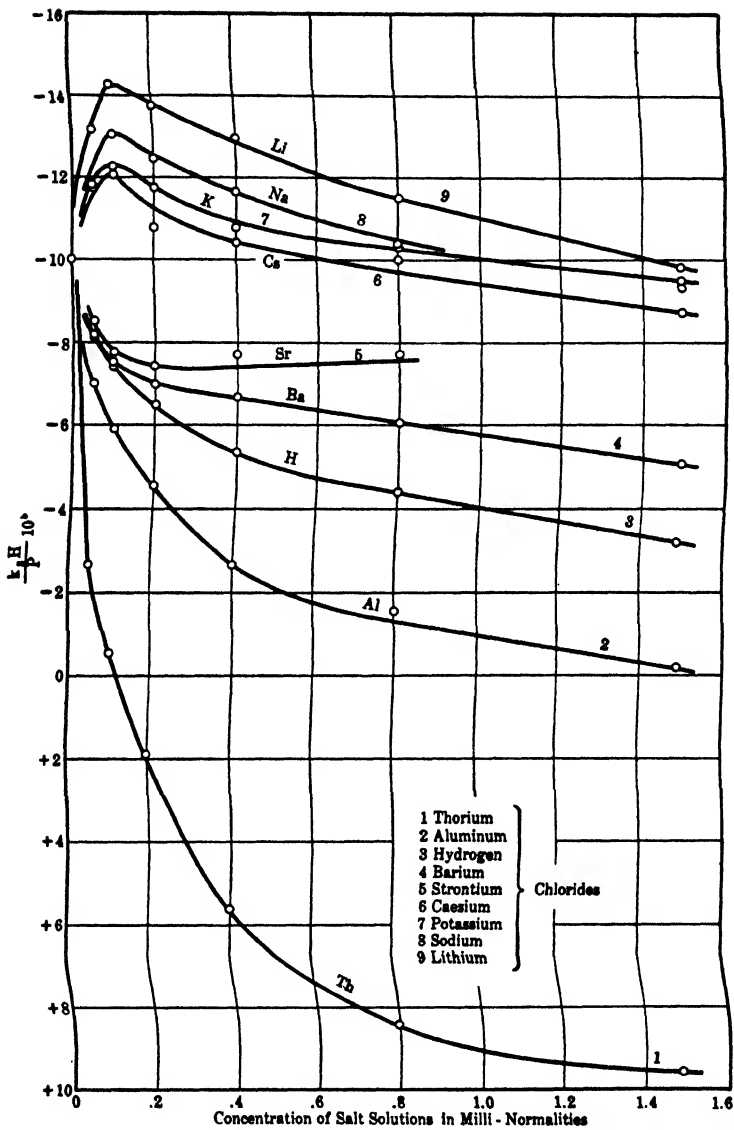
FIG. 8. INFLUENCE OF CATION CHLORIDES UPON THE ζ–POTENTIAL AT CELLULOSE–WATER INTERFACE. (Briggs.)

report a specific volume of 0.64 (density = 1.56), and density values ranging from this down to 1.50 are generally agreed upon. It is of interest that the same cellulose immersed in water appeared to have a specific volume of 0.621, and this apparent contraction is usually attributed to the strongly bound water having an abnormally high density, although the authors believe that water may have penetrated certain vacuoles not permeable to helium. Values in acetone (0.642) and in benzene (0.644) are practically the same as in helium, but the same cellulose immersed in water and then treated so that acetone displaced the water without drying gave 0.618. This smaller volume following the water treatment may indicate an actual contraction of the cellulose structure with closing up of some space between the crystallites. Such an apparent contraction of water applies only to the first 3 to 4 per cent taken up; beyond that it has normal density.

Because of the pore space, the density of the common woods varies widely; balsa 0.12 to 0.20, spruce 0.48 to 0.70, Douglas fir 0.44 to 0.51, loblolly pine 0.64, and ebony 1.1 to 1.3. Commercial wood pulps range from 1.41 to 1.63, while cotton hairs show values from 0.77 to 1.05, and papers may vary from 0.7 to 1.15. From such figures it is possible to estimate the percentage of pore space in a specimen. For cotton hairs this appears to be 32 to 41 per cent.

The specific heat of pure cellulose from cotton is given as 0.319, while that of mechanical wood fiber is 0.327 as compared with 0.319 for sulfite and 0.323 for soda pulps; the impurities present therefore appear to have little effect. Heat is conducted better along the fiber axis than at right angles to it, and the heat conductivity is affected by the relative pore volumes. Forty years ago Vignon[40] reported heats of combustion as follows: for purified cotton (dried at 110°) 4223 calories per gram, cellulose precipitated from Schweitzer's reagent 3982 calories, mercerized cellulose 3980 calories, oxycellulose 4124 calories, and sucrose 3955 calories. Common woods give 4600 to 5000 calories per gram. More recent values are 4293 calories per gram for high-grade bleached rag stock and 4284 calories per gram for purified bleached sulfite pulp.

Optical Properties. Among the optical properties of cellulose, the property of double refraction is of most interest. Ramie, the best-oriented native fiber, has an axial index of refraction of 1.595, a transverse refraction of 1.534, and consequently a double refraction of 0.061. Less perfectly oriented cotton showed 1.580, 1.534, and 0.046 for the respective values. From the latter data, Preston calculated that the fibril structure was wrapped around the fiber axis at an angle of 30°.

Since cellulose is not known to dissolve in any solvent in the purely

physical sense, its properties in the dissolved state are not known, but solutions of its degradation products and its derivatives do rotate the plane of polarized light. With wavelengths of light below 3300 Å, paper, filter paper, viscose, and cellulose acetate fluoresce strongly, whereas cellulose nitrate is practically without this property.

Electrical Properties. The electrical conductivity of cellulose fibers depends to a considerable degree on their history, as that affects moisture and ash contents. In general, fibrous materials are good electrical insulators, but Stamm showed that, as wood increased in moisture content from 7 to 30 per cent (the moisture saturation point), the conductivity increased over a hundred thousandfold. As water was added up to the completely water-filled condition (150 to 300 per cent), conductivity increased only about twentyfold. In papers to be used for insulation purposes, low ash content, high temperature of drying, and maintenance in low humidities all help to reduce the conductivity. The actual conductivity includes both bulk and surface conductivity. In distilled water the latter may be ten to twenty times the former, and beating pulp increases the surface conductivity in the order of 50 per cent. Recent experiments show that the dielectric constant of cellulose is about 6.1.[10]

Mechanical Properties. The theoretical ultimate strength of primary valence chains of cellulose is calculated as 800 to 2260 kg. per sq. mm. as compared with 170 kg. for the best steel. Although no fiber approaches either of these ideal values, the latter of which Hermans[18] has since exploded, the high orientation of flax enables it to show over 100 kg. per sq. mm. Other values quoted by Stamm[37] include in the same units: well-oriented viscose 80, paper (unit solid fraction and maximum orientation) 30, cotton 28, ordinary viscose 25, wood 8 to 15, and paper 0.5 to 8.0. It is believed that natural fibers fall so low in this scale because of the relative shortness of the chains in the macro sense, so that the rupture comes on the bonds between the crystallites and groups of crystallites and between the fibers themselves.

RECENT LITERATURE ON CELLULOSE

No attempt has been made in this chapter to list specific references in detail. Frequently concepts developed are the sum of contributions by many authors, and the current developments are followed best by the aid of *Chemical Abstracts* or the " Bibliographies of Paper Making " by C. J. West. Sections of interest in this connection will be found also in the " Reports of the Progress of Applied Chemistry " issued annually by the Society of Chemical Industry (British) and the " Annual Survey of American Chemistry," the last edition of which appeared in 1935.

Recent books of interest include: Marsh and Wood, " An Introduction to the Chemistry of Cellulose," published by Chapman and Hall, London, 1938; E. Hägglund, " Holzchemie," Akad. Verlag., Leipzig, 1939; H. Mark, " Physik und Chemie der Cellulose," Springer, Berlin, 1932; C. G. Schwalbe, " Die Chemie der Hölzer," Borntraeger, Berlin, 1938 (this is the first of four volumes designed as a second edition to his well-known textbook); and A. G. Norman, " The Biochemistry of Cellulose, the Polyuronides, Lignin, etc.," Oxford, Clarendon Press, 1937. The excellent " Outlines of Biochemistry," by R. A. Gortner (Wiley, 1938) provides colloidal background.

Several articles summarizing aspects of the cellulose field have been published recently. " Survey of American Literature in the Field of Cellulose and Related Subjects, 1933 through 1937 " was given by H. F. Lewis in Volume 107 of *Paper Trade Journal* for 1938. Under the title " Cellulose Research 1933-37 " L. E. Wise published three articles in *Paper Industry* for 1938. Late in 1935 E. Heuser published three installments on " The Nature of Cellulose, A Historical Review " in Volume 101 of the *Paper Trade Journal*. The pamphlet " Colloid Chemistry of Cellulosic Materials " by A. J. Stamm, published as *Miscellaneous Publication* 240 of the United States Department of Agriculture, 1936, gives a splendid summary of the colloidal properties.

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CHAPTER II

FIBROUS RAW MATERIALS

E. Sutermeister

The Vegetable Cell. The vegetable cell is the structural unit of the plant fabric. It varies in shape, structure, and arrangement among different plants and even among different parts of the same plant. These variations in the cell depend, in general, on its function in the plant and give rise to such cell structures as fibers, ray cells, and ducts.

In the higher forms of plants the cell consists of protoplasm and cell wall. The protoplasm is composed of a rather viscous, water-white, transparent liquid and granular solids. It is a complex albuminoid material, similar to the white of egg in appearance and composition. The cell wall develops from the protoplasm. At first it consists of a thin, homogeneous film which envelopes the protoplasm, but it soon becomes modified in appearance and composition according to its function.in the plant.

Most cells continue to retain their affinity for water, sometimes absorbing it so freely as to form a thick mucilage on warming. Some, however, become cutinized or suberized and then are said to be waterproof, like those in cork. Still other cells, like those in grasses, become mineralized with calcium, magnesium, boron, silicon, etc., which adds to the strength and stiffness of the plant. In addition, some plant cells are further modified by lignification, which further stiffens and strengthens the plant and also increases the adhesion between adjacent cells. The lignin forms in the early life of the cell and is closely associated with the hemicellulose and cellulose. It is highly concentrated in the hemicellulose at the periphery of the cell, and is less concentrated in the cellulose, which forms the major portion of the cell wall. The hemicellulose at the wall periphery is dissolved with the lignin during the preparation of pulp from wood.

Thickening of the cell wall of wood fibers occurs simultaneously with the formation of the cellulose; it takes place in about 12 days in some woods,[26] which is about one-fourth of the time required for cotton fibers to mature. The thickening process takes place rather unevenly and causes markings such as stratifications, striations, depressions, and pits in the cell wall, which can be employed for the identification of

fibers from different plant materials. The stratifications and striations indicate the demarcation between the concentric sleeves and the fibrils of the cell wall,[22] and the depressions and pits in the wall are avenues for the transmission of sap from fiber to fiber.

In many plants, gums and resins are formed by rather obscure processes which are probably in large part degradations of the cell walls. The products of such changes are often found as small, irregular solids or drops, either within the cells or in the spaces, known as resin ducts, arising from the confluence of a number of cells. In general the gums are soluble in water and can be hydrolyzed by acids to simple sugars. The resins are soluble in alcohol or in solutions of the alkalies; they are colored reddish orange by a solution of Sudan III in dilute alcohol and when thus strained may be readily recognized under the microscope.

Only the living cells contain protoplasm, and these are found at the points where growth is taking place. The older cells, where growth has ceased, occasionally contain a little water but generally only air, more or less highly rarefied. They are still of value in the plant structure for the stiffness and strength which they impart. Cells are present in different plants in an almost infinite diversity of form, but, except for those which aid in the identification of the fibers which they accompany, the following discussion will be confined to the long, slender, pointed elements of the bast or woody tissues, which, with the exception of cotton, are the only ones of practical interest to the paper maker. Such fibers are derived from the ordinary cells simply by growth and change of form.

The paper-making fibers may be divided, according to their source, into four classes:

1. Seed hairs, of which cotton is the only representative.

2. Bast fibers, such as hemp, flax, and manila.

3. Those derived from whole stems, such as straw, esparto, or bamboo, which are associated with various cells and vessels that are not properly fibers.

4. Fibers derived from wood.

SEED HAIRS

Cotton (*Gossypium*). The cotton fiber consists of a single hairlike cell which, when fully ripe, is flattened and twisted. This appearance is characteristic of fully matured cotton but not of unripe fiber or that which has been injured during growth. The fibers form the covering of the cotton seed and are removed from it by ginning. Their length

varies from 2 to 5.6 cm., and their diameter from 0.0163 to 0.0215 mm.; the longest fibers are found in the Sea Island cottons, followed by Egyptian, Brazilian, American, and East Indian. The cell walls of the mature cotton are thin and often present a granulated appearance or highly characteristic cross markings.

Cotton reaches the paper mill in the form of rags and spinning waste. Cotton hull fiber, or " linters," which are the short fibers removed from the seed by mechanical processes, are also occasionally available and can be used in high-class papers. Linters can usually be distinguished from the fibers prepared from rags by their microscopic appearance. Many are not flattened and twisted but are more nearly cylindrical, with very thick walls and small central canals. Linters are used chiefly in the preparation of cellulose solutions for lacquers and similar products; its preparation as a paper-making fiber is discussed briefly in Chapter III.

For an analysis of raw cotton, as well as for analyses of a number of the bast and whole-stem fibers, see Table 2. These analyses are from Müller[13] and, though old, were made by the same methods, and so are at least comparable. The more modern analyses are made by different methods and frequently show different constituent groups, hence they do not aid the reader in comparing one raw material with another.

BAST FIBERS

This class includes the fibers found in the inner bark of various plants, often in the form of bundles of considerable length. It is these fiber bundles or filaments which are of particular interest in textile work, while the paper maker is concerned only with the ultimate fibers composing these filaments. The fibers are usually firmly attached to those above and below them by incrusting matters or by partial identity of their cell walls, so that chemical treatment is generally necessary in separating them. The filaments, on the other hand, are isolated from the surrounding tissues by various mechanical or chemical processes, one of the commonest being retting as applied to flax and hemp.

The walls of bast fibers are usually of considerable thickness, and the central canal varies greatly in the different species and even in different individuals of the same species. The irregularities of the cell walls may take the form of thickenings or knots, projections into the cell cavity or outward from the walls, or other peculiar deformations. Variations in the lignification and in the nature of the materials deposited in and on the cell walls are often so characteristic as to assist materially in their identification.

Linen.   Linen is composed of the bast fibers of the flax plant, *Linum usitatissimum*.   The plant yields about 8 per cent of fiber, which is separated by retting and is then known as flax.   The ultimate fibers are 6 to 60 mm. long and 0.012 to 0.026 mm. wide, with an average ratio of length to width of about 1200.   They are thick-walled tubes with thickened places or knots at intervals.   The ends are tapered, the walls rather transparent, and the canal small.

Linen reaches the paper mill as scutching waste, spinning refuse, threads, rags, etc.   It requires much the same treatment as is given to cotton except that a rather more severe bleaching process is necessary.   Many attempts have been made to utilize the flax straw remaining when the seed is grown for oil production, but so far without success.

Hemp (*Cannabis sativa*).   The fiber is prepared by retting, from filaments which run the entire length of the stem.   The ultimate fibers composing the filaments vary from 5 to 55 mm., averaging about 22 mm. long and 0.022 mm. in diameter; the ratio of length to diameter is about 1000.   The fibers have very thick walls which are not very highly lignified.   The ends are large and sometimes flattened, and the central canal is almost obliterated.   In microscopic appearance the fibers are very similar to those of flax; they show the same knots or thickenings and the same striae, but they differ from linen in having more ability to break down into fibrillae during the mechanical processes of paper making.

Many other plants yield fibers to which the name hemp is given, but they are generally distinguished as manila hemp, sisal hemp, sunn hemp, etc.

Hemp comes to the paper mill in the shape of rags, rope, and cordage. It is used in high-grade papers, particularly very thin sorts, where its ability to split into fibrillae makes it especially valuable.

Manila Hemp (*Musa textilis*).   This fiber is prepared by stripping, scraping, and drying, from the outer sheath of the stems of a plant of the banana family, known in the Philippines as abaca.   The ultimate fibers are from 3 to 12 mm. long and average about 6 mm.; the width varies from 0.016 to 0.032 mm. with an average of 0.024 mm.   They taper very gradually toward the ends; the central canal is large and very prominent, and fine cross markings are numerous.

The paper maker obtains manila fiber chiefly as old ropes and cordage.   It is generally given a light alkaline treatment with lime and used in the unbleached condition for papers where strength is far more important than cleanliness or color, but it is occasionally bleached to a light yellow.

Jute (*Corchorus capsularis* and *C. olitorius*). The filaments are obtained by retting or maceration and are used in the manufacture of twine, cordage, and woven goods such as burlap. It is in these forms and also as " butts " and " rejections " that it reaches the paper maker.

The fibers of jute are about 2 mm. long and 0.022 mm. in diameter. They are thick-walled, and the central canal varies from a considerable width to hardly more than a line. The surface is quite smooth and at intervals shows radial canals and joints similar to those in linen, though not so pronounced. As used in paper making the fibers are not completely separated, so that bundles of fibers are of frequent occurrence.

Jute was regarded by Cross and Bevan as typical of lignified fibers. They considered it a chemical entity, which they termed lignocellulose, and which they thought split up into cellulose and other products on treatment with suitable reagents.

Paper Mulberry (*Broussonetia papyrifera*). These fibers are used by the Japanese in some of their peculiar papers. They are separated from the inner bark of the tree by scraping, soaking, and maceration in water, and are sometimes purified still further by boiling in weak alkaline solutions. As used in Japanese papers the fibers are generally unbroken. They are long and slender, varying in length from 6 to 20 mm., with an average width of 0.030 mm. They are nearly transparent when viewed under the microscope, and show transverse jointings as well as longitudinal striae. The central canal generally shows as a well-defined line, and the ends are sometimes blunt and rounded and sometimes **fringed.**

Agave. These fibers are prepared from the leaves of various species of agave by maceration or scraping. The filaments thus obtained are light colored, lustrous, and comparatively stiff. Among the most common fibers of this class is henequen or sisal hemp, which is largely employed for cordage, bags, etc., in which form it reaches the paper mill. The ultimate fibers are long, slender, tapering, and pointed at the ends. The central canal is not prominent but can be seen as a narrow line in some of the fibers. The walls are thick and are characterized by many fine cross lines, close together, which are found on nearly every specimen. The fibers are harsher than paper mulberry and longer than manila.

FIBERS DERIVED FROM WHOLE STEMS

The fibers in this class are produced from the entire stems and so include the ultimate fibers from all the structural elements of the stem proper and also cells from the epidermis and other parts of the plant.

Straw.   In straw pulp the bast fibers form the greater part of the pulp.   These are comparatively short and slender with sharp pointed ends, and at intervals the walls are thickened and drawn together to resemble joints.   The dimensions of straw fibers vary with the kind of straw and with the conditions of growth, nature of soil, etc.   They are longer than those from esparto but not so long as those from spruce wood, and compare more nearly with poplar fiber in paper-making value.

Accompanying the bast fibers in straw pulp are numerous epidermal cells with serrated edges, and also smooth, thin-walled cells, from the pithy portion of the stem, varying in shape from nearly round to long, oval cells whose length is several times their width.   Both types of cell aid materially in the identification of straw pulp.

Esparto (*Stipa tenacissima* and *Lygeum spartum*).   The bast fibers are grouped in bundles or filaments which are resolved into ultimate fibers by the chemical processes employed.   The fibers are shorter and more even than those from straw, averaging about 1.5 mm. in length, and the central canal is nearly closed.   Serrated cells are numerous but considerably smaller than those from straw, while the smooth, thin-walled cells are absent.   The chief characteristic which distinguishes esparto from other fibers is the presence of small tear-shaped cells derived from the hairs on the surface of the leaves.

Bamboo.   Bamboo fibers resemble those from the straws in many of their characteristics.   According to Raitt[14] the average length of the ultimate fibers is from 2.20 to 2.60 mm. according to the variety, and the diameters are from 0.018 to 0.027 mm.   Though not so long as spruce fibers they are much longer than those from any of the deciduous trees.   Accompanying the true fibers are numerous serrated cells and ovoid pith cells of various sizes and shapes.   Cells similar to the tear-shaped cells of esparto have also been noticed.   Many of these cells are very small, and a good proportion is lost during the preparation of the pulp.

The number of species of bamboo runs into the hundreds, not all of which are suited for paper making because of the difficulties in reduction to pulp and bleaching to good color.

Rushes.   In many districts there are large areas of swampland densely covered with rushes of various kinds.   The fibers in these are very similar to esparto, and pith cells are also present though they are far smaller than those from straw and many would be lost during the washing and bleaching processes.

Examination of rushes from South Carolina showed that they contained 35 per cent of cellulose, of which about 30 per cent con-

sisted of fine pith cells which would wash easily through a 100-mesh sieve.

TABLE 2

Analyses of Fibrous Raw Materials[13]

	Cotton	Belgian Flax		Italian Hemp	Manila Hemp	Jute	
		1	2			Cuttings	Colorless
Cellulose.............	91 15	82.57	71.50	77 77	64 72	61 74	64 24
Incrusting substances, etc.... ..	....	2.74	9 41	9.31	21 83	21 29	24 41
Water..............	7.56	8 65	10 70	8 88	11 85	12.58	9.93
Fat and wax........	0.53	2.39	2.37	0 56	0 63	0.45	0.39
Ash...............	0.11	0.70	1 32	0 82	1 02	....	0.68
Water extract.	....	3 65	6.02	3 48	0 97	3 94	1.03
Nitrogen........ .	0 67	....	....	....	.. .	....	....

	China Grass	Wheat Straw	Rye Straw	Bamboo	Esparto	
					Spanish	African
Cellulose.............	78.07	49.17	49.22	52.84	50.19	50.16
Incrusting substances, etc...... .	6 10	30 34	27 70	26 17	27.23	28 83
Water...............	9 05	10 39	11.75	9 63	9.75	8.45
Fat and wax...........	0.21	1 58	1.99	0 83	2 15	2.51
Ash..................	2 87	....	....	5.13	3.72	3.34
Water extract...........	6.47	8.52	9.34	11.13	10.68	10.05

Rushes appear to require a more drastic cooking treatment than straw or esparto, and the fibers bleach a little harder. They are, however, potential sources of fiber should necessity arise, and it is understood that Danube reeds are already employed as a substitute for esparto in Europe.

Bagasse and Corn Stalks. These two materials are so similar in their fibrous characteristics and in the cooking treatment necessary that they may be considered as practically identical. The seven states in the " corn belt " produce annually about 80 million tons of corn stalks, the greater part of which is practically a waste. Bagasse, the crushed stalks of the sugar cane, is produced in large quantities in the sugar industry. It was formerly utilized as a fuel, though its value was low because of the large amount of water present; more recently it has found considerable use in making insulating and wall boards.

The fibers in both these materials include long, thick-walled fibers, shorter ones of similar structure, and cells of various shapes and sizes, such as serrated cells of comparatively large size, long thick cells with rounded ends, and many pith cells with such thin walls that nearly all collapse and become flat during the reduction process. These pith cells are much larger than those in straw and hence much more difficult to remove by washing. Their presence has proved to be one of the chief obstacles to the use of either bagasse or corn stalks, since fiber containing them imparts hardness and rattle to the paper which are undesirable in many products.

Canes. Cuban cane, Brava cane (*Gynerium sagittatum*), and giant cane (*Arundinaria macrosperma*) are potential sources of cellulosic material, resembling bamboo in many respects.. Cuban cane will yield a high-grade pulp by the soda process, while for giant cane the sulfate process gives the best results, with a yield of about 50 per cent on the dry basis. The pulp can be easily fractionated into two approximately equal portions, one consisting of almost pure long bast fibers, and the other containing shorter fibers with a larger proportion of pith cells, but still suitable for use in paper and boards.

Miscellaneous Materials. In this class are almost innumerable materials which have been proposed from time to time. Papyrus which grows in immense quantities along the Nile is said to yield about 33 per cent of easy bleaching pulp by the soda process.[2] Also mentioned are the trimmings from fruit trees and grape vines; asparagus[16] waste from canning factories and dry stalks at the end of the season; pea and bean vines,[17] which according to Reinke yield better fiber than asparagus; cotton stalks, of which immense quantities are burned every year, but which so far have never been utilized successfully; zacaton, a Mexican grass, which has been carefully investigated by the Bureau of Plant Industry;[4] tropical grasses, numerous species of which have been tried on an experimental scale by Raitt,[15] Richmond,[20] and others. Many of these have been found to produce excellent fiber.

Peat also might possibly be considered in this class. Numerous attempts have been made to utilize it, the treatments ranging from an entirely mechanical process, through cooking with alkalies and acids, to fermentation processes. All methods have thus far failed to produce a fiber which can be used in anything but the coarsest products.

WOODS

It is well recognized that pulp can be produced from nearly any fibrous raw material, but no source of cellulose has yet been discovered which can equal wood, either in suitability for the many types of paper, or in cheapness of pulp per unit weight.

The woody tissues of plants are made up of cells which exhibit great diversity of form, size, and markings, as Figs. 9 and 10 show. Those in which the paper maker is particularly interested are the true wood
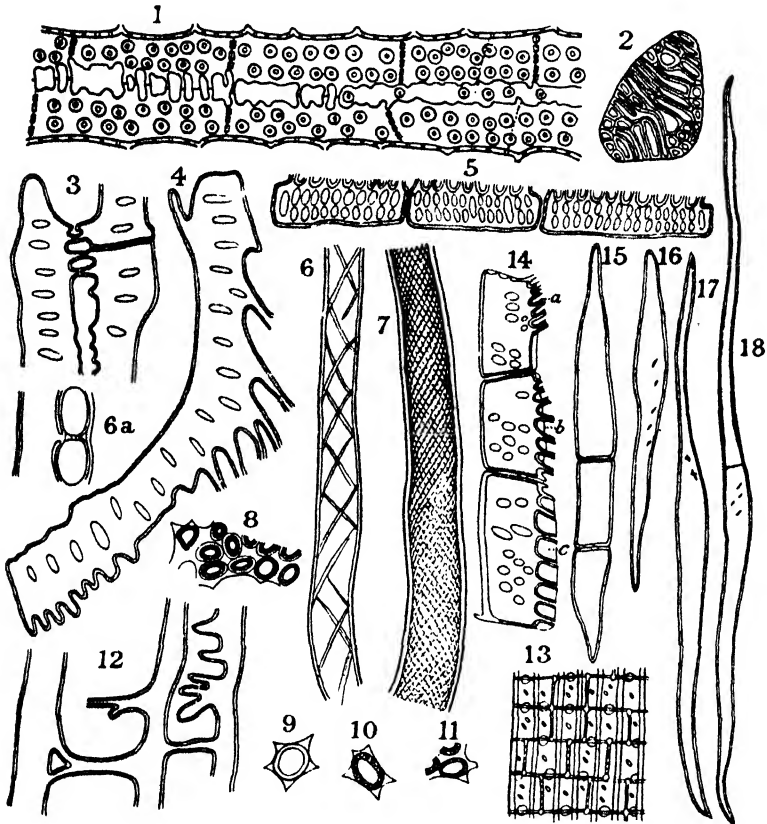
FIG. 9. DRAWINGS OF WOOD ELEMENTS

1–7. *Avicennia* sp. 1. Wood-parenchyma cells; tangential section. 2. Septum of a duct. 3, 4, 5. Conjugate wood-parenchyma cells. 6, 7. Portions of spirally striated libriform fibers. 8–11. Bast cells of *Cytisus laburnum*. 8. Cross section through young bast bundle acted on by chloroiodide of zinc. 9, 10, 11. Cross sections through young bast cells similarly treated. 12. *Porlieria hygrometrica;* radial section of conjugate substitute fibers. 13. *Jatropha manihot*, radial section through wood. 14–18. *Tectona grandis;* elements separated by maceration. 14. Conjugate wood-parenchyma cells. 15. Ordinary wood-parenchyma fiber. 16. Substitute fiber. 17. Libriform fiber. 18. Septate libriform fiber.

fibers, or libriform cells, and the tracheids. The wood fibers are always spindle or fiber-form, and the walls are relatively strongly thickened.

They never have true spiral striations; in only a few species do they
show pits, which are generally elongated and oblique.   Wood fibers
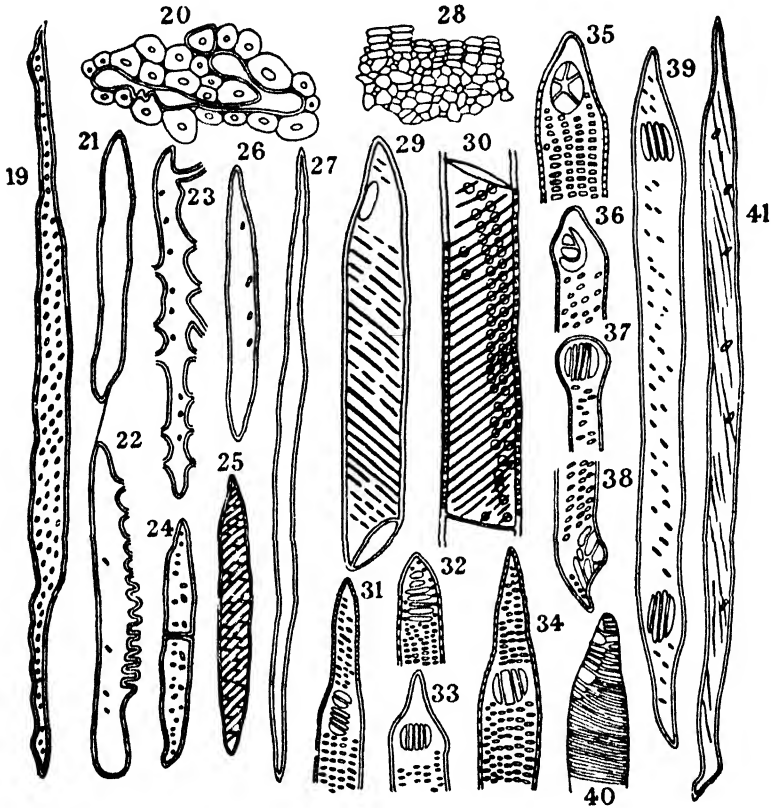
FIG. 10.   DRAWINGS OF WOOD ELEMENTS

19.   Tracheid from *Tectona grandis*.   20–23. *Porlieria hygrometrica*.   20. Con-
jugate substitute fibers in cross section.   21. Ordinary substitute fiber after macera-
tion.   22, 23. Conjugate substitute fibers after maceration.   24–27. *Cytisus labur-
num;* elements after maceration.   24. Wood-parenchyma fiber.   25. Tracheid.   26.
Substitute fiber.   27. Simple libriform fiber.   28. Cross section through cambium
and youngest wood of *Cytisus laburnum*.   29, 30. *Mahonia aquifolium;* ducts.   29.
After maceration.   30. Longitudinal section.   31–36. Extremities of ducts sepa-
rated by maceration from *Hieracium*.   37–39. Ducts from *Onopordon acanthium*.   40.
Spirally marked duct from *Vitis vinifera*.   41. Libriform fiber from *Jatropha manihot*.

are variable in length in different woods, ranging from 2.0 mm. to 0.14
mm., but in all cases they are the longest elements present.   As an

example of wood fibers may be cited the chemical pulp made from poplar wood; this contains in addition only the ducts and a few of the small cells from the medullary rays.

Tracheids are elongated and tapering cells, more or less lignified and having peculiar markings known as bordered pits or discoid markings. Figure 11 shows these as they appear on the surface of the fiber and illustrates how they are formed by the thin partition wall between two tracheids. These pits are so constant in number and mode of distribution that they may serve as a distinguishing characteristic for some
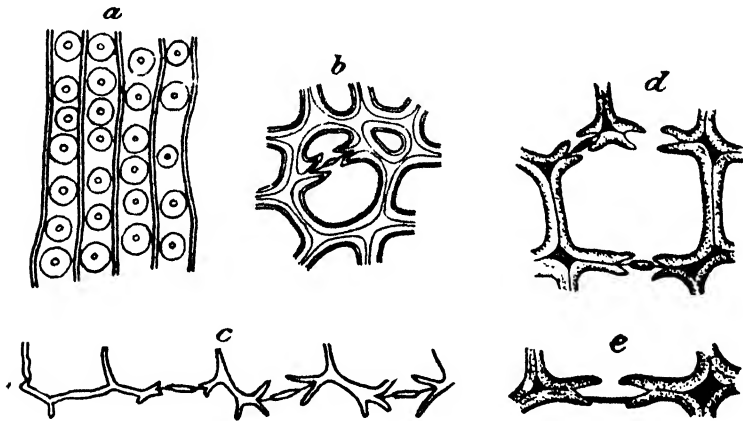
FIG. 11. DISCOID MARKINGS ON WOOD CELLS

Pinus laricio; a. Radial walls; *b.* A transverse section.
Pinus sylvestris; c. Development of markings; *d, e.* Transverse sections of nearly perfect and perfect discoid markings.

woods. In coniferous trees, such as spruce, fir, and hemlock, the wood consists almost entirely of tracheids, and when sulfite fiber or groundwood from such trees is examined under the microscope the discoid markings may be readily seen. These tracheids are generally much longer than the libriform fibers from other woods and hence possess greater paper-making value.

Sap- and Heartwood. Sapwood, or that of comparatively recent growth, is usually lighter in color and contains more fermentable material than the older and denser heartwood. Each year a layer of sapwood changes into heartwood and becomes darker and harder from infiltration of coloring matters, resins, etc. Sapwood is generally preferred for pulp because it is more easily reduced by both mechanical and chemical processes. In some woods, as fir and buckeye, there is

no difference in color and hardness between heartwood and sapwood.

When cooks were made under the same conditions, Hägglund found that wood from different parts of the trunk and branches gave different yields and qualities of fiber. The middle of the trunk gave about 1 per cent higher yield than wood from the top of the log, while the branches gave about 10 per cent lower yield, owing to more rapid cooking. If the cook is shortened a normal yield is obtained, but the fiber is weak compared with that from the log.

Springwood and Summerwood. Bray and Curran[5] made a most interesting study of growth conditions of southern yellow pines as related to the quality of fiber produced and found the most important single factor to be the ratio of springwood to summerwood. Springwood fibers are thin walled and collapse into flat ribbons, thus tending to produce dense, closely knit, well-formed paper with a smooth surface. Summerwood fibers, on the other hand, are thick walled and needlelike; they do not collapse and so give bulky paper of uneven formation and rough surface characteristics. As the proportion of springwood increases, the pulps give higher bursting and tensile strengths, but lower tearing resistance, and so are better for making printing and wrapping papers, where density, good formation, smoothness of surface, and high bursting and tensile strengths are essential. For coarse papers where bulk, porosity, and resistance to tear are desirable the wood used should contain a high percentage of summerwood.

From similar studies of sulfite pulps Chidester, McGovern, and McNaughton[7] have concluded that a variation of 10 per cent in the springwood content of any one species of wood will result in a greater difference in pulp quality than is exhibited between the different species of southern pine examined.

Fiber Length. Mell[12] studied the length of tracheids from coniferous woods and found that it varied considerably, not only in different parts of the same tree, but also within the same annual ring at the same distance above the ground. In both trunk and branches the average length increases from the center outward until the tree reaches its maximum height, after which it remains quite constant. The highest average length of tracheids in the branches is usually less than in the trunk. Tracheids also vary in length with the character of the soil and the amount of moisture available, those from trees growing in rich, moist soil being longer than those from trees grown in dry soil. Lee and Smith[11] made similar studies of one or two trees of Douglas fir, and their observations confirm, in general, those of Mell, though their conclusions differ in some respects.

TABLE 3

Name of Tree

Name of Tree	Average Fiber Length in millimeters		
	1	2	3
Conifers			
Balsam fir (*Abies balsamea*)	3.10	...	2.7
White fir (*Abies concolor*)	4.63	2.5	3.5
Alpine fir (*Abies lasiocarpa*)	3.16	2.4	...
Noble fir (*Abies nobilis*)	4.02	4.4	...
Port Orford cedar (*Chamaecyparis lawsoniana*)	3.63	3.4	2.6
White cedar (*Chamaecyparis thyoides*)	2.10	3.8	2.1
Western larch (*Larix occidentalis*)	2.59	4.4	2.6
Incense cedar (*Libocedrus decurrens*)	4.01	3.2	2.0
White spruce (*Picea glauca*)	3.53	3.4	2.8
Engelmann spruce (*Picea engelmanni*)	5 71	...	3.0
Red spruce (*Picea rubra*)	2.97	2.6	3.7
Jack pine (*Pinus banksiana*)	5.06	...	2.5
Sugar pine (*Pinus lambertiana*)	4 47	4.4	4.1
Silver pine (*Pinus monticola*)	4.39	5.2	..
Lodgepole pine (*Pinus contorta*)	2.63	...	2.3
Longleaf pine (*Pinus palustris*)	5.53	...	3.7
Western yellow pine (*Pinus ponderosa*)	3.32	3.3	3.6
Pitch pine (*Pinus rigida*)	3.86	4.0	...
White pine (*Pinus strobus*)	3.53	3.9	4.1
Loblolly pine (*Pinus taeda*)	3.10	5.4	3.0
Virginia pine (*Pinus virginiana*)	2.73	...	2.8
Douglas fir (*Pseudotsuga taxifolia*)	2.68	2.6	4.4
Redwood (*Sequoia sempervirens*)	6.99	6.4	5.5
Southern cypress (*Taxodium distichum*)	4.69	6.5	3.3
Arborvitae (*Thuja occidentalis*)	2.02	2.2	...
Hemlock (*Tsuga canadensis*)	4.01	3.2	3.0
Western hemlock (*Tsuga heterophylla*)	3.04	...	2.7
Broad-leaved woods			
Aspen (*Populus tremuloides*)	1.15	...	1.0
Largetooth aspen (*Populus grandidentata*)	1.08	1.3	1.1
Beech (*Fagus grandifolia*)	1.13	1.2	1.1
Red alder (*Alnus rubra*)	1.23	...	1.2
Sycamore (*Platanus occidentalis*)	1.57	1.6	1.7
Tupelo gum (*Nyssa aquatica*)	1.85	1.4	1.6
Black gum (*Nyssa sylvatica*)	1.68	...	1.7
Red gum (*Liquidamber styraciflua*)	1.55	...	1.6
Red maple (*Acer rubrum*)	0.93	...	0.8
White maple (*Acer saccharinum*)	....	0.6	...
Buckeye (*Aesculus glabra*)	0.63	0.9	...
Cucumber magnolia (*Magnolia acuminata*)	0.86	1.6	1.3
Yellow poplar (*Liriodendron tulipifera*)	1.14	2.3	1.8
American elm (*Ulmus americana*)	1.35	1.1	1.6
Basswood (*Tilia americana*)	....	1.1	1.1
Paper birch (*Betula papyrifera*)	1.17	...	1.2
Yellow birch (*Betula lutea*)	....	1.7	1.5

* Data in column 1 for conifers are from Mell: *Paper Trade J.*, June 15, 1911; those for broad-leaved wood are from measurements by the author. Columns 2 and 3 are from Record: " Timbers of North America," and from *Bulletin* 1485 of the United States Department of Agriculture, respectively.

Because of these variable factors it is very difficult to determine the average lengths of tracheids, or of libriform cells in broad-leaved woods, and wide differences may be expected between any observed fiber length and that given as the average for the particular type of wood under observation.   Even the averages given by different authorities are often far from consistent, as is seen from Table 3, which shows average figures from four different sources.

Moisture in Wood.   The cell cavities of woods contain large amounts of air and moisture.   According to Sachs the volume percentage of freshly cut fir wood is:

	Per Cent
Cell walls	24.81
Water	58.63
Air cavities	16.56

The moisture in wood varies with the amount of seasoning, the kind of wood, the position in the tree, and the time of cutting.   In the living tree certain kinds of wood, such as white ash, black locust, and the white and red cedars, are comparatively dry; black ash and the oaks have about twice as much moisture, and chestnut and buckeye about three times as much as white ash; cypress and white fir also contain large amounts of water.   In the hardwoods the variation in moisture with the different positions in the tree is comparatively slight, but the conifers show wide variations, the heartwood generally being very dry and the sapwood very wet.

Seasoning greatly reduces the amount of moisture present in wood, but the rate of drying is not the same for all varieties, some losing moisture in a tenth of the time required by others.   The term " air dry " therefore, is one which may denote almost any condition of moisture from 40 per cent down to 4 per cent of the total weight, according to the length of seasoning and the conditions to which exposed.

Weight per Cubic Foot.   The weight per cubic foot of wood is closely related to its moisture content, since the shrinkage in volume due to loss of moisture is not at all proportional to the amount lost. To be of comparative value it is therefore best to base the weight per cubic foot on the absolutely dry material.

The following figures for the oven-dry weight of woods per cubic foot of green volume have been taken from *Technical Note* 218 of the United States Forest Service.   In considering these it must be understood that the density of wood of the same species varies so greatly that only approximately average figures can be given.

TABLE 4

Kind of Wood	Pounds, Oven-Dry per Cubic Foot Green Volume
Alder, red (*Alnus rubra*)..........................	23.1
Aspen (*Populus tremuloides*).......................	21.8
Aspen, largetooth (*Populus grandidentata*)..........	21.8
Basswood (*Tilia glabra*)..........................	20.0
Beech (*Fagus grandifolia*).........................	34.9
Birch, gray (*Betula populifolia*)......	28.0
Birch, paper (*Betula papyrifera*)......	30.0
Birch, yellow (*Betula lutea*)......................	34.3
Chestnut (*Castanea dentata*)	25.0
Cottonwood, eastern (*Populus deltoides*).......	23.1
Douglas fir (*Pseudotsuga taxifolia*), coast type	28.1
Fir, balsam (*Abies balsamea*).	21.2
Fir, lowland white (*Abies grandis*).........	23.1
Fir, noble (*Abies nobilis*)............	21.8
Fir, red (*Abies magnifica*)...........	23.1
Fir, silver (*Abies amabilis*)...	21.8
Fir, white (*Abies concolor*).......................	21.8
Gum, black (*Nyssa sylvatica*)...............	28.7
Gum, red (*Liquidamber styraciflua*).	27.4
Gum, tupelo (*Nyssa aquatica*)	28.7
Hemlock, eastern (*Tsuga canadensis*).	23.7
Hemlock, western (*Tsuga heterophylla*)..............	23.7
Magnolia, cucumber (*Magnolia acuminata*)..........	27.4
Maple, red (*Acer rubrum*)	30.5
Maple, silver (*Acer saccharinum*)...................	27.5
Maple, sugar (*Acer saccharum*).....................	35 6
Pine, jack (*Pinus banksiana*)......................	24.4
Pine, loblolly (*Pinus taeda*).......................	31.2
Pine, lodgepole (*Pinus contorta*)...................	23.7
Pine, longleaf (*Pinus palustris*)....................	34.4
Pine, northern white (*Pinus strobus*)................	21.3
Pine, Norway (*Pinus resinosa*).....................	27.5
Pine, pitch (*Pinus rigida*)........................	28.1
Pine, shortleaf (*Pinus echinata*)...................	30.6
Pine, Virginia (*Pinus virginiana*)...................	26.0
Poplar, balsam (*Populus balsamifera*)	18.8
Poplar, yellow (*Liriodendron tulipifera*)..............	23.7
Spruce, black (*Picea mariana*)....................	23.7
Spruce, Engelmann (*Picea engelmanni*)..............	19.4
Spruce, red (*Picea rubra*).........................	23.7
Spruce, white (*Picea glauca*)......................	23.1
Sycamore (*Platanus occidentalis*)...................	28.7
Tamarack (*Larix laricina*)........................	30.6
Willow, black (*Salix nigra*)	21.2

Resins. Many woods contain small amounts of volatile oils generally approaching terpene ($C_{10}H_{16}$) in chemical composition. Practically nothing is known regarding their formation. From these by oxidation are formed balsams and resins, the balsams being regarded

as mixtures of resins with volatile oils. Some resins contain gum or mucilage and are hence termed gum resins.

There is no positive knowledge regarding the actual amount of resin in wood because it varies greatly with the different solvents used in its determination. Different woods also contain quite different amounts of extractible matter, and though the hardwoods are not generally considered resinous it will be seen from the proximate analyses that many of them contain as much alcohol-soluble material as the softwoods. With Canadian woods Richter[21] obtained the following results:

	Ether Extract	Alcohol Extract
	Per cent	Per cent
Fresh balsam	0 45-0.85	1 15-3.65
Fresh spruce........	0 70-1.80	0 70-1.94

Examination of the resins obtained gave the following constants:

	Ether Resin		Alcohol Resin	
	Acid Number	Saponification Number	Acid Number	Saponification Number
White spruce............	61	80	54	83
Black spruce............	66	110	35	168

Richter claims that storage of the wood decreases the ether extract and increases the alcohol extract, while Schwalbe and Grimm[31] state that seasoning or passing air over the chips reduces both ether- and alcohol-soluble material.

The ether extract is usually lighter in color and more liquid and sticky than the alcohol extract. Part of each is soluble in petroleum ether, and according to Johnsen[10] it is this portion which is responsible in large part for the trouble with pitch in sulfite pulp. The portion soluble in petroleum ether is a thick yellow liquid and appears to be of a fatty rather than a resinous nature; the insoluble part is brown and brittle.

The resin in Bohemian pine and its distribution in the sulfite cellulose made from it have been studied by Sieber,[32] who found that cooking removed 4.2 per cent; the knotter, screens, sand traps, etc., 51.8 per cent, while bleaching removed 15 per cent.

The resins in sulfite pulps are generally found to be present as small particles within the ray cells, and if these are removed by washing or fractioning, the pulp will cause much less trouble.

Proximate Analysis of Wood. Table 5 gives the analyses of a number of European woods.[30]

<div align="center">TABLE 5</div>

Component	Spruce (*Picea excelsa*)	Pine (*Pinus silvestris*)	Beech (*Fagus silvatica*)	Birch (*Betula verrucosa*)	Poplar (*Populus tremula*)
	Per cent	Per cent	Per cent	Per cent	Per cent
Ash.........................	0.77	0.39	1.17	0.39	0.32
Fat (ether extract)...............	0.78	1.92	0.31	0.71	1.08
Wax (alcohol extract)............	1.52	1.53	1.47	1.09	2.08
Protein (N × 6.25)..............	0.69	0.80	1.05	0.74	0.63
Pentosans......................	11.30	11.02	24.86	27.07	23.75
Methyl pentosans................	3.00	2.23	1.02	0.84	0.72
Cellulose containing pentosan.....	63.95	60.54	67.09	64.16	62.89
Cellulose, pentosan-free...........	57.84	54.25	53.46	45.30	47.11
Lignin.........................	28.29	26.35	22.46	19.56	18.24

Still more complete analyses of seven American woods are given by Schorger,[29] all percentages being based on samples dried at 105° C. His results are in Table 6.

The percentages of cellulose given in this table by Schorger are considerably higher than the figures of most other analysts for the same or similar woods. They are probably more accurate because of the more complete knowledge of the precautions necessary to prevent hydrolysis of the cellulose and its consequent loss during the analytical procedure. Other analyses of woods are given by Ritter and Fleck,[23] who also made analytical studies of springwood and summerwood,[24] and heartwood and sapwood.[25]

Bark and Knots. The bark serves as a protective envelope for the stem and gradually increases in thickness, as a layer is added each year. It contains long bast fibers which give it strength, cork cells, which are impermeable and hence form a protective covering for the tissues beneath, and often coloring matters and tannins, sometimes in sufficient amounts to make extraction profitable. It is only slightly acted on by the chemical processes of pulp making and so interests the paper maker chiefly because of the necessity for its removal. The loss in barking varies greatly with the size and shape of the logs, with the care used in operating the barkers, and with the type of barker

TABLE 6

| Wood | Ash | Solubility of Wood in | | | Acetic Acid by Hydrolysis | Methoxyl Groups | Pentosans | Cellulose |
		Hot Water	Ether	1 Per Cent NaOH				
Longleaf pine (*Pinus palustris*)	0.37	7.15	6.32	22.36	0.76	5.05	7.46	58.48
Douglas fir (*Pseudotsuga taxifolia*)	0.38	6.50	1.02	16.11	1.04	4.95	6.02	61.47
Western larch (*Larix occidentalis*)	0.23	12.59	0.81	22.14	0.71	5.03	10.80	57.80
White spruce (*Picea glauca*)	0.31	2.14	1.36	11.57	1.59	5.30	10.39	61.85
Basswood (*Tilia americana*)	0.86	4.07	1.96	23.76	5.79	6.00	19.93	61.24
Yellow birch (*Betula lutea*)	0.52	3.97	0.60	19.85	4.30	6.07	24.63	61.31
Sugar maple (*Acer saccharum*)	0.44	4.36	0.25	17.64	4.46	7.25	21.71	60.78

used. With disk barkers it may amount to 10 to 25 per cent of the rough wood.

Bark is regarded by the pulp maker as an unavoidable nuisance. Attempts have been made to substitute it for better materials in making roofing felts and similar products, but compared with the total amount produced such use is very small. Probably the best means of disposing of bark is to burn it for fuel. Rue and Gleason[27] found its heating value to vary from 8560 to 10,820 B.t.u. per pound, oven-dry. If the bark is removed by disk barkers and is relatively dry, burning involves no serious problems, but if it is removed by wet drum barkers it is too wet to burn and the excess moisture must be removed by drying or by some form of press. There are several types of presses which are able to reduce the moisture in the pressed bark to 50 per cent, and the advantage gained is claimed to more than offset the cost of the press and its maintenance.

Knots are formed at the points where the branches protrude from the trunk. They are usually very hard and dense and frequently highly charged with resins and coloring matters. They are partially reduced to pulp by the soda process, but are usually not even softened by the sulfite process.

Decay. The increasing cost of wood makes the importance of decay more and more apparent, but positive evidence is almost unobtainable because there is no way to measure the degree to which the wood has been affected. The problem has therefore been attacked by studying the conditions tending to prevent decay in stored wood and by determining the effect of decay on the yield and physical properties of the fiber.

If the wood is sound when received, certain precautions may be taken to prevent or minimize decay. The chief factor influencing decay is the moisture in the wood; if this amounts to 60 per cent of the total weight little decay will occur, and the same is true if the moisture is very low. High moisture content can be obtained and maintained in the wood yard by continuously spraying the piles with water; this also reduces the fire risk to almost nothing. The other extreme is best assured by piling the wood in small, evenly stacked piles which permit good ventilation and rapid drying, but even this method is not entirely satisfactory because of dependence on weather conditions. According to Blair[3] the limiting conditions of moisture are shown by the fungus *Lenzites sepiaria,* which grows on coniferous woods when comparatively dry, and by *Fomes roseus,* which grows in cool, wet locations.

Other precautions which minimize decay are the careful removal of old bark, decayed wood, etc., from the yard. New wood should never be piled on such a foundation but whenever possible crushed stone, gravel, or cinders should be used. Spraying the foundation with a disinfectant is also recommended by Haas.[9]

The results of using decayed wood in pulping apparently depend on the process used. If the wood is so badly rotted that it is friable, much of it may be lost during chipping and screening, so that yields based on a cord of original wood will be abnormally low by any process. Rue, Miller, and Humphrey[28] have shown that in the sulfite process the yields, both on the weight and volume basis, were not much lower than from sound wood. Apparently for newsprint sulfite the amount of decay which can be tolerated is considerably greater than is usually supposed.

In the soda process using poplar and hardwoods the yields and quality of the fiber are considerably more affected than in preparing sulfite. The bleach required rises rather sharply with increasing decay, and the strength of the fiber and its ability to withstand beating drop.

The chemical pulping processes sterilize the pulp and prevent further decay unless reinfection takes place, but with groundwood no such sterilization is effected and decay frequently continues to a serious extent in the stored product. This can be prevented only slightly by

selection of wood or removal of rotten portions, because decay may be well started before it becomes marked enough to justify culling the wood.

After a study of decay in groundwood Richards[19] recommends that a preservative treatment be given by spraying with one of the three following mixtures, the quantities being for 1 ton of air-dried pulp:

1. Cymene 4 lb., naphthalene 1 lb., betanaphthol $\frac{1}{2}$ lb.
2. Cymene 4 lb., naphthalene 1 lb., paradichlorbenzene $\frac{1}{2}$ lb.
3. Cymene 6 lb., naphthalene $1\frac{1}{2}$ lb.

More recent and more toxic chemicals which have been recommended for this work are Dowicide H (sodium tetrachlorophenoxide) and Lignasan (ethyl mercuric chloride). According to Rennerfelt[18] practical trials of this last have not been entirely successful, possibly because of uneven distribution, and its profitable use is still questionable.

Study of the problem of decay has shown that different fungi affect the yield and quality of fiber very differently. Since it is impossible to measure the degree of decay in wood or to estimate with any accuracy the proportion of affected wood in a pile it has never been possible to measure the effect of decay with any degree of exactness, but as early as 1920 it was estimated by the Forest Service that the damage to groundwood alone amounted to five to fifteen million dollars annually.

Dead Wood. The use of dead timber for pulping is frequently brought into question because of the quantities available after serious forest fires or insect infestations. Information on this phase of pulping is difficult to find, but Cameron and Lodge[6] state that fire-killed spruce and balsam gave good grades of sufite pulp after satisfactory adjustments were made in the cooking conditions. With both fire-killed and insect-killed woods the problem seems to be whether it can be obtained and used before serious decay has taken place, and whether it can be satisfactorily cleaned from the charred places, etc.

Kinds of Wood. The woods most generally used in the United States are spruce, balsam, and hemlock for sulfite; poplar and hardwoods for soda; southern pines for sulfate; and spruce for groundwood. Other woods are used for all these processes in quantities depending on such factors as fiber length, color, ease of reduction, cost, and the location of the mill with regard to its wood supply. In the following pages are mentioned some of the woods which are in actual use or which have been tried out sufficiently on an experimental scale to demonstrate their value. The names and ranges of the various species

have been taken from Sudworth's " Check List of the Forest Trees of the United States "; the other data have been collected from widely scattered sources.

Spruces. Red spruce, *Picea rubra,* ranging from Nova Scotia to North Carolina and Tennessee, and white spruce, *Picea glauca,* are the common pulpwoods of the East. The white spruce ranges from Newfoundland to Hudson Bay, northwestward to Alaska, and southward to northern New York, Michigan, Wisconsin, Minnesota, South Dakota, Montana, and British Columbia. Both woods are light, soft, straight grained, and fairly free from resin. Very similar in quality are Engelmann spruce, *Picea engelmanni,* ranging from northern Arizona through the Rocky Mountain region to British Columbia, and Sitka spruce, *Picea sitchensis,* extending in the coast region from Alaska to northern California. This latter species is now rated third in desirability as a west coast pulpwood, western hemlock and the true firs being considered superior.

All the spruces pulp easily by the sulfite or sulfate process but with considerably more difficulty by the soda process, which gives fiber very hard to bleach. The uniformly light color of the wood makes all well suited for the preparation of groundwood; Sitka spruce, however, is somewhat inferior to the others in color.

Firs. Balsam fir, *Abies balsamea,* occurs from Newfoundland and Labrador westward to the region of Great Bear Lake and southward to Pennsylvania. Its wood is very light, soft, not strong, rather coarse grained, and not durable. It is often cut and used with spruce for making sulfite pulp, but its fiber is considered somewhat inferior and is likely to contain more pitch. Balsam fir can be used successfully in the preparation of groundwood of good color, but its use is not favored because of the low yield per cord and its tendency to decay.

Other firs which are found largely on the Pacific coast and in the Rocky Mountain region are lowland fir, *Abies grandis;* white fir, *A. concolor;* silver fir, *A. amabilis;* noble fir, *A. nobilis,* and red fir, *A. magnifica.* The wood of most of these is light, soft, and straight grained; it varies in the different species from fine to moderately coarse grained. All these trees grow to comparatively large size and yield excellent pulpwood. With the proper treatment all can be cooked satisfactorily by the sulfite process with the production of long fiber similar in quality to that of spruce, and all can be used for preparing groundwood for newsprint, though the color of the product is usually rather inferior to that from spruce.

Pines. The bulk of the pine wood available in the southern states consists of four varieties: longleaf pine, *Pinus palustris;* shortleaf pine,

P. echinata; loblolly pine, *P. taeda*; and slash pine, *P. caribaea.* In general these range from southern Virginia to Florida and eastern Texas and northward to northeastern Alabama and northwestern Georgia. The wood of these pines varies greatly in density, rate of growth, and relative proportions of spring- and summerwood. A typical average sample of pulp from these pines contains about 60 per cent of fibers from the springwood and 40 per cent from summerwood.

The sapwood of most pines is easily reduced by the sulfite process, but the heartwood is much more resistant. Other pines which give a fair quality of fiber by the sulfite process are jack pine, lodgepole pine, Norway pine, pond pine, sand pine, and Virginia pine. Jack pine and pond pine tend to give more screenings than the others because the uniformity of digestion is not so good.

Excellent mechanical pulp may be made from northern white pine, limber pine, piñon pine, and sugar pine, and from the sapwood of many of the southern pines.

The chief use of the southern pines has been in the sulfate process for the production of strong, long-fibered, unbleached stock for wrapping and kraft papers; modern methods of bleaching are now making the fibers available for white or light-colored papers.

Hemlock. Eastern hemlock, *Tsuga canadensis,* ranges from Nova Scotia to Minnesota, Wisconsin, Michigan, and southward in the mountains of the Atlantic region to northern Alabama and Georgia. Western hemlock, *T. heterophylla,* has a range from Alaska to Idaho and Montana and southward in the Cascade and coast mountains to California.

Both woods are light, soft, brittle, and not durable; their color is light brown tinged with red.

Eastern hemlock is used to a considerable extent in the sulfite process; it yields fiber very similar to spruce, though the treatment has to be rather more severe. It also gives a good grade of kraft fiber, and a fair grade of groundwood can be made from it, though with more difficulty than from spruce. Western hemlock is superior to the eastern variety for both sulfite and groundwood and is one of the most important pulpwoods on the Pacific Coast.

Larch or Tamarack (Larix laricina). Larch ranges from Newfoundland and Labrador to northern Pennsylvania, Indiana, Illinois, central Minnesota, and northwestward to Hudson Bay.

The wood is very heavy, hard, strong, rather coarse grained, durable in contact with the soil; color light brown, the sapwood nearly white.

Larch is reduced by the sulfite process with some difficulty, and if

The following photomicrographs show the characteristic forms and markings of a number of the typical paper-making fibers. These photomicrographs were prepared by the Paper Section of the Bureau of Standards.
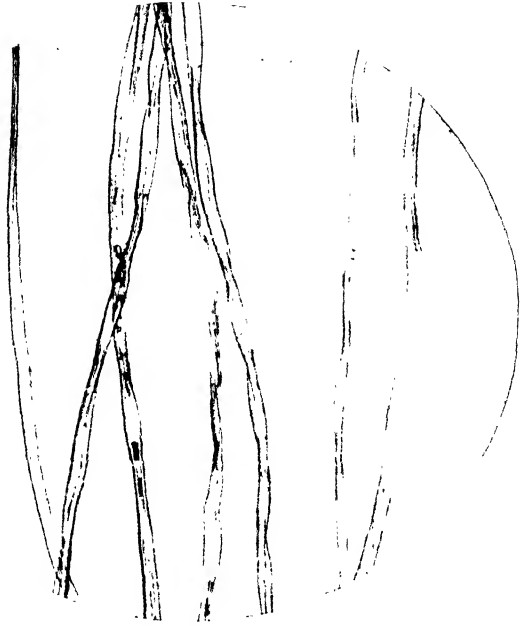
Cotton (*Gossypium*). Magnification 100 diameters. Photographed by Bureau of Standards.

Linen (*Linum usitatissimum*). Magnification 100 diameters. Photographed by Bureau of Standards.

Plate 1

Hemp (*Cannabis sativa*). Magnification 100 diameters. Photographed by Bureau of Standards.

Manila (*Musa textilis*). Magnification 100 diameters. Photographed by Bureau of Standards.

PLATE 2
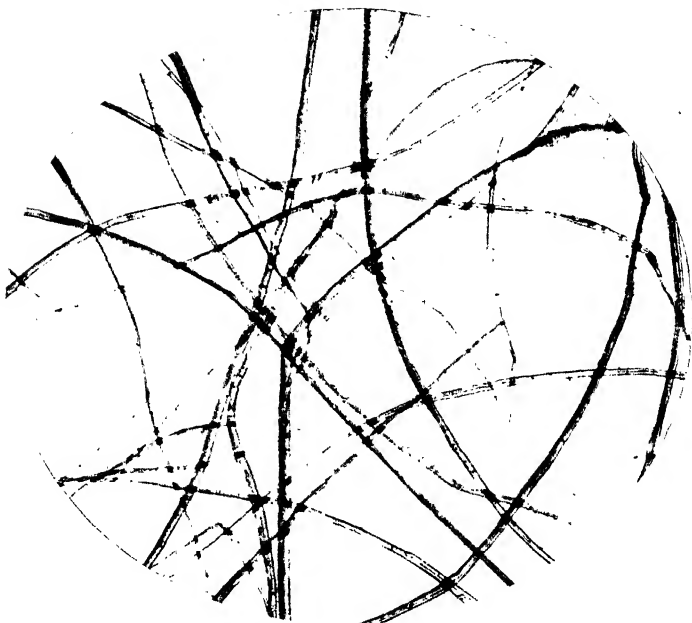
Jute (*Corchorus capsularis*)   Magnification 100 diameters.   Photographed by
Bureau of Standards.

Paper Mulberry (*Broussonetia papyrifera*).   Magnification 100 diameters.
Photographed by Bureau of Standards.

PLATE 3

Sisal (*Agave rigida*). Magnification 100 diameters. Photographed by Bureau of Standards.

Rice Straw (*Oryza sativa*). Magnification 100 diameters. Photographed by Bureau of Standards.

PLATE 4

Esparto (*Stipa tenacissima*). Magnification 100 diameters. Photographed by Bureau of Standards.

Bamboo (*Bambusa arundinacea*). Magnification 100 diameters. Photographed by Bureau of Standards.

PLATE 5

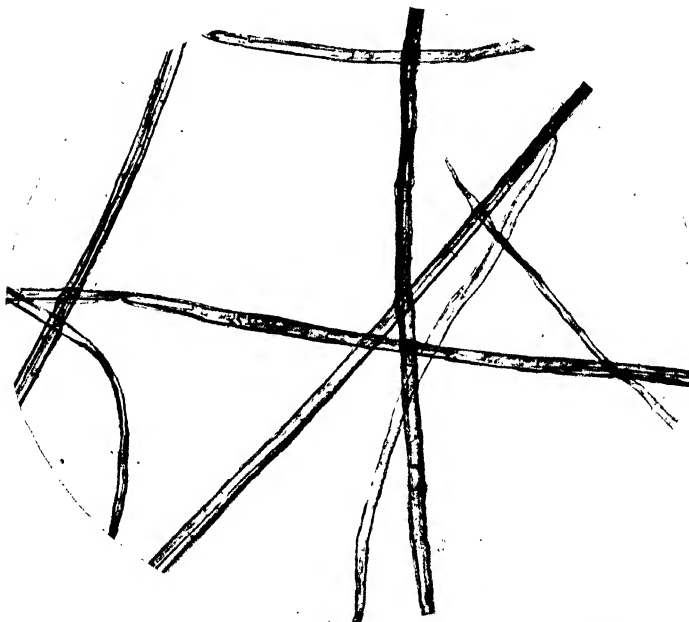Corn (*Zea mays*). Magnification 100 diameters. Photographed by Bureau of Standards.
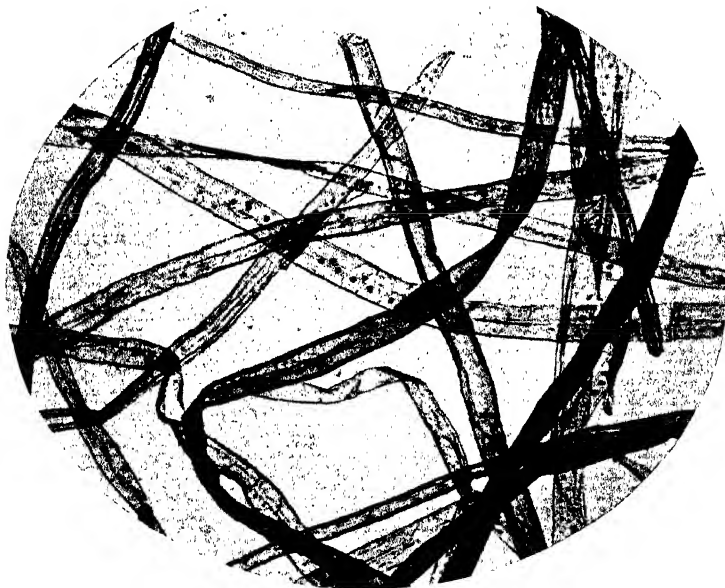
Red Spruce (*Picea rubens*). Magnification 100 diameters. Photographed by Bureau of Standards.

PLATE 6

Spruce Ground Wood (*Picea canadensis*). Magnification 100 diameters. Photographed by Bureau of Standards.
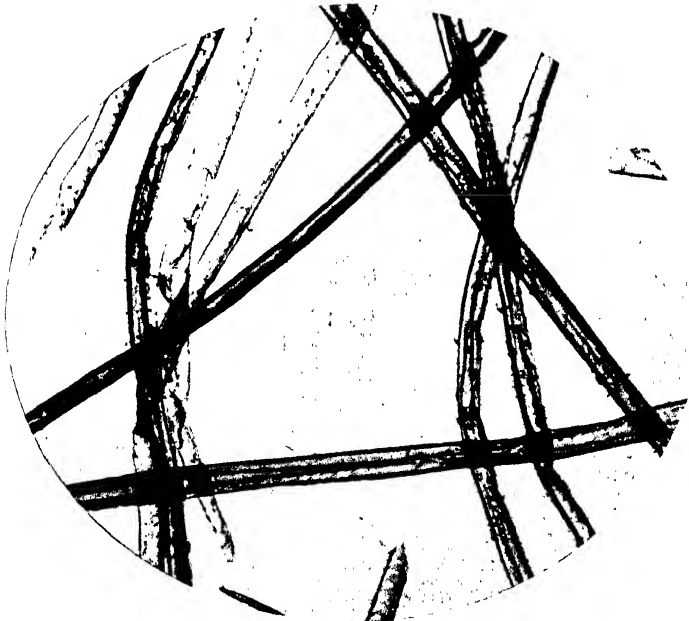
Balsam Fir (*Abies balsamea*). Magnification 100 diameters. Photographed by Bureau of Standards.

PLATE 7
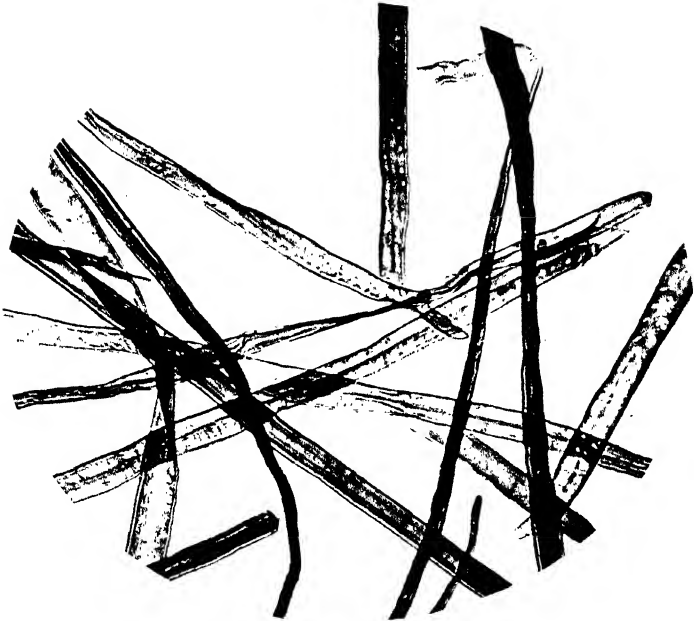
Jack Pine (*Pinus divaricata*). Magnification 100 diameters. Photographed by Bureau of Standards.
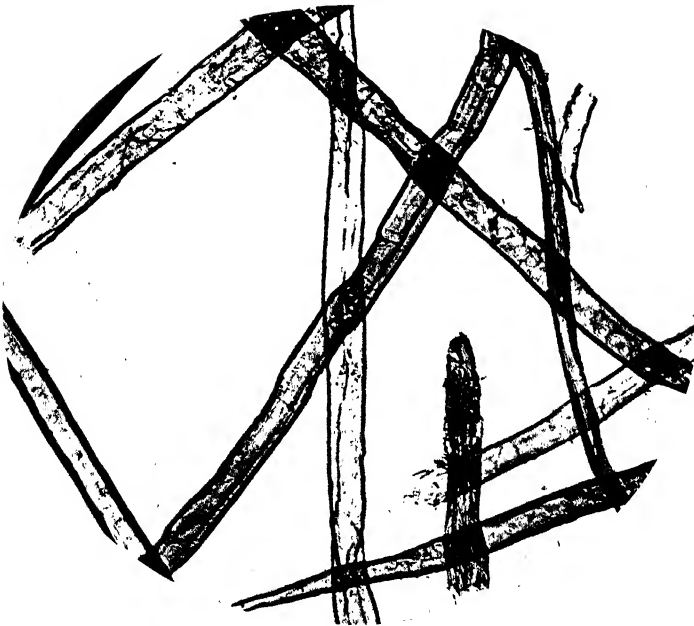
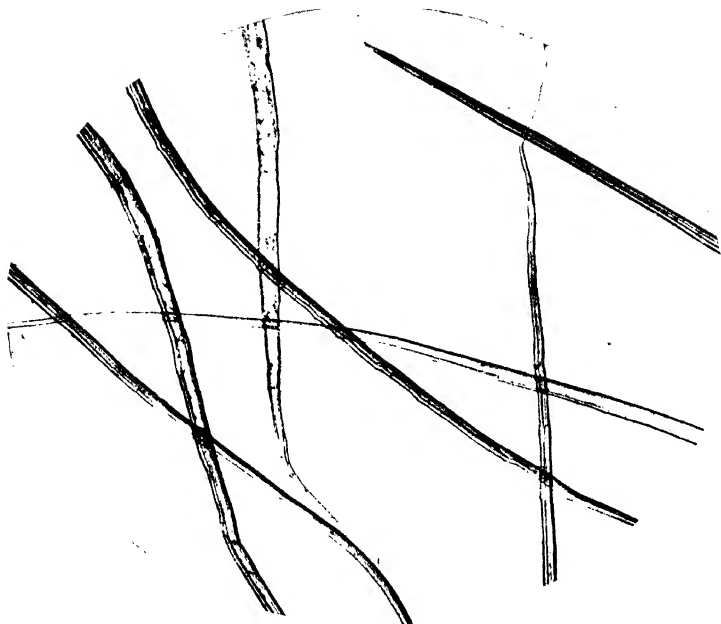Hemlock (*Tsuga canadensis*). Magnification 100 diameters. Photographed by Bureau of Standards.

PLATE 8
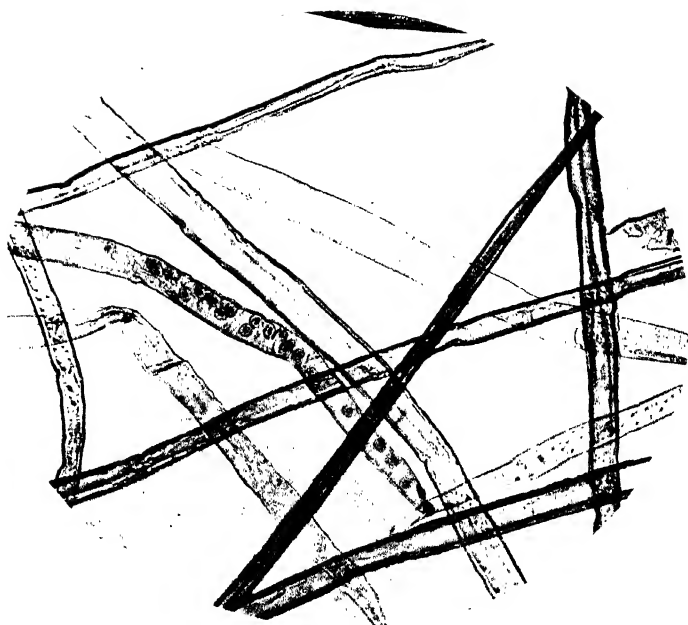
Douglas Spruce (*Pseudotsuga taxifolia*). Magnification 100 diameters.
Photographed by Bureau of Standards.

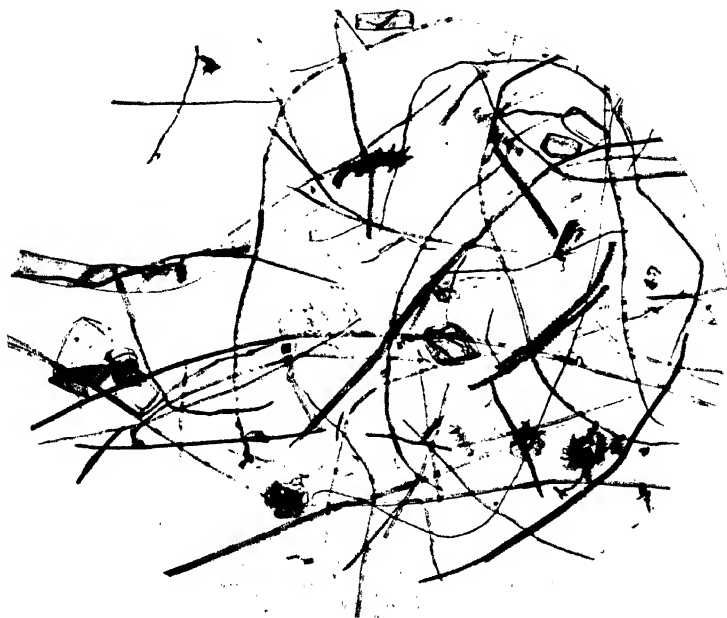Aspen (*Populus tremuloides*). Magnification 100 diameters. Photographed by
Bureau of Standards.

PLATE 9
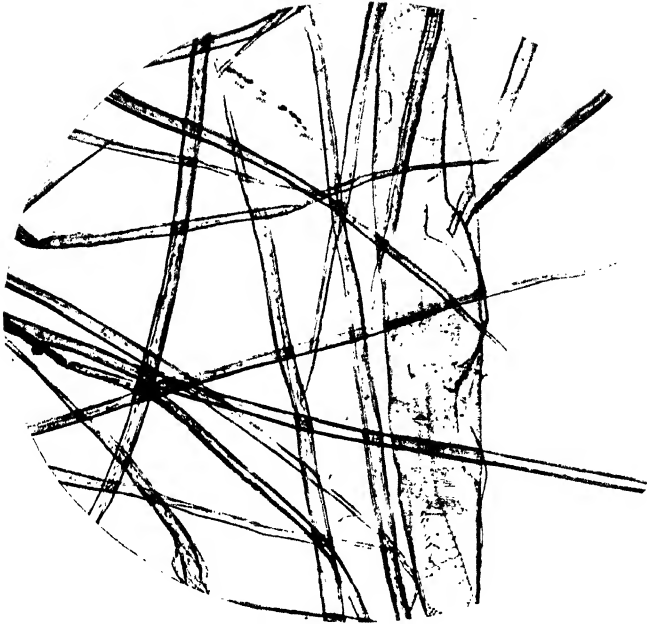
Yellow Birch (*Betula lutea*). Magnification 100 diameters. Photographed by Bureau of Standards.

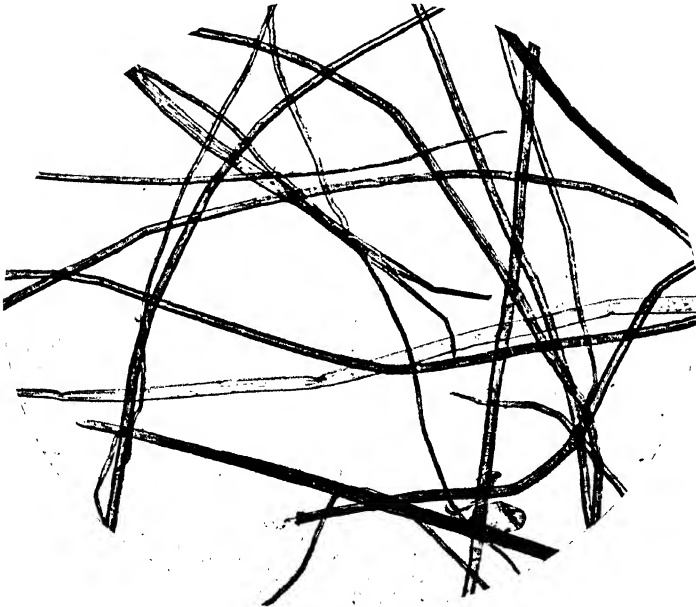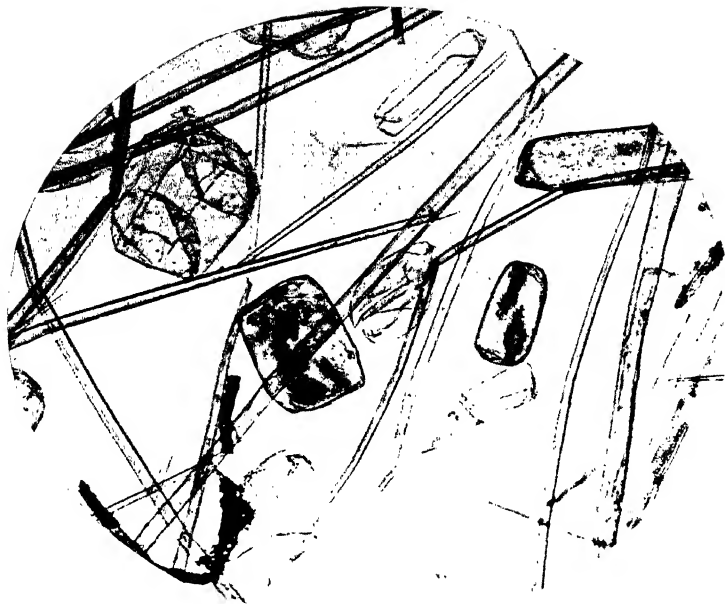Beech (*Fagus atropunicca*). Magnification 100 diameters. Photographed by Bureau of Standards.

PLATE 10

Chestnut (*Castanca dentata*). Magnification 100 diameters. Photographed by Bureau of Standards.

Tulip-tree (*Liriodendron tulipifera*). Magnification 100 diameters.
Photographed by Bureau of Standards.

PLATE 11

Sweet Gum (*Liquidambar styraciflua*). Magnification 100 diameters.
Photographed by Bureau of Standards.

Hard or Sugar Maple (*Acer saccharum*). Magnification 100 diameters.
Photographed by Bureau of Standards.

PLATE 12

Soft or Silver Maple (*Acer saccharinum*). Magnification 100 diameters. Photographed by Bureau of Standards.

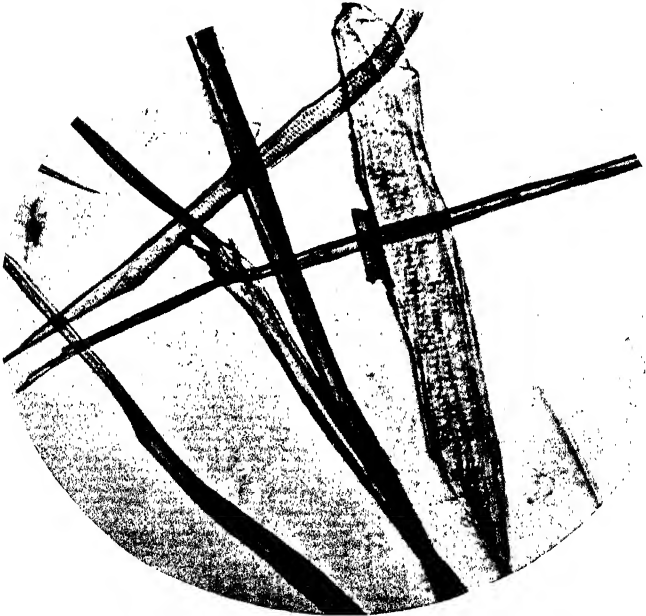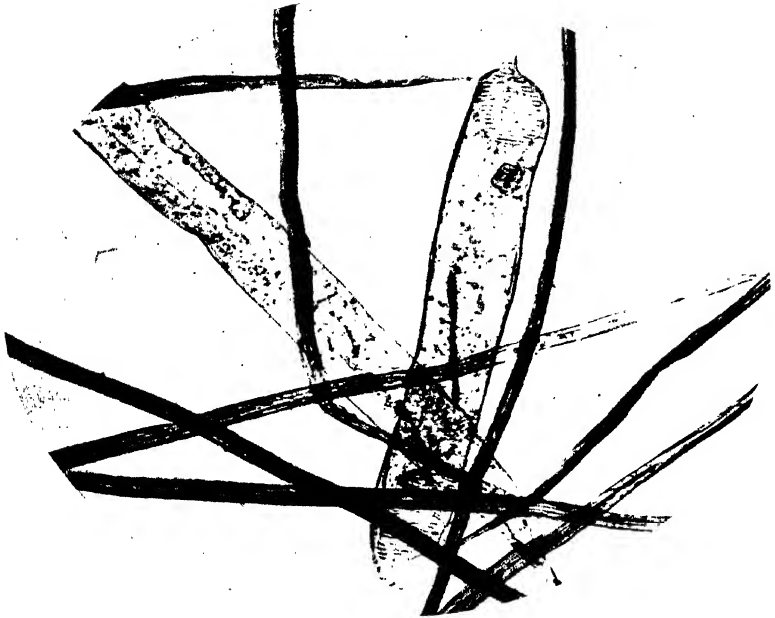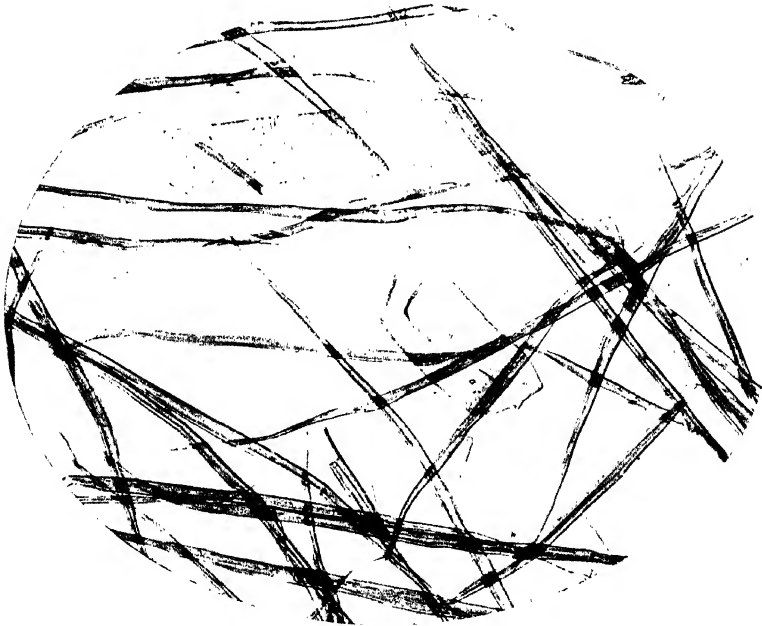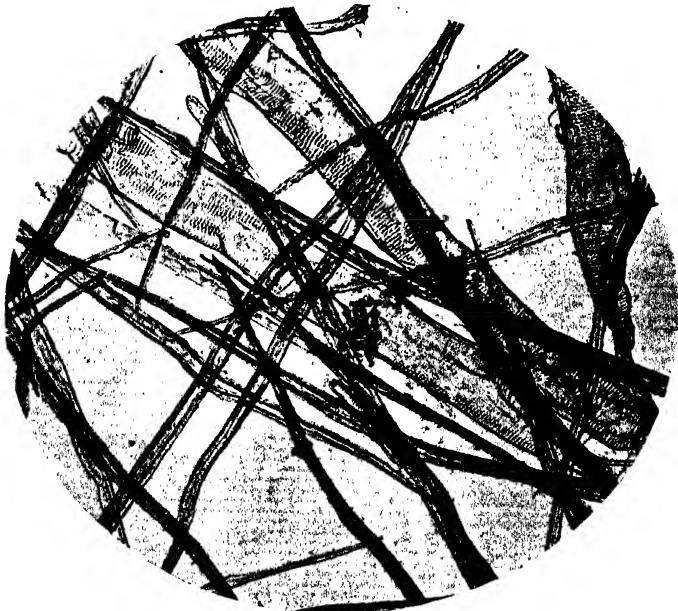Black Gum (*Nyssa sylvatica*). Magnification 100 diameters. Photographed by Bureau of Standards.

PLATE 13

mixed with spruce or hemlock it is apt to cause chips and shives. By the sulfate process it can be made into a good grade of kraft fiber, and it also yields groundwood of good quality except for color, which is a decided grayish green.

Douglas Fir (Pseudotsuga taxifolia). Ranges from the Rocky Mountain region northward to central British Columbia.

The wood varies widely in character and grain, which may be very coarse, medium, or fine. The coarse-grained wood is usually reddish brown; the fine-grained, clear yellowish brown. The wood is slightly resinous and resembles pine in many of its characteristics.

Douglas fir is well suited for making kraft pulp; it is probably not used at the present time for sulfite pulp, though it can be reduced fairly well under certain conditions of pulping. The fiber is comparatively dark colored, though bleachable for certain grades of paper.

Largetooth Aspen (Populus grandidentata). Ranges from Nova Scotia through New Brunswick, southern Quebec, and Ontario to northern Minnesota; southward to Delaware, southern Indiana, and Illinois.

The wood is light, soft, not strong, close grained, compact, decays rapidly; color light brown, the sapwood nearly white.

This is the wood most commonly used in the soda process; it is seldom used in sulfite mills though it is readily reduced by that process. It yields a groundwood of fair color but of rather short fiber, suitable for special grades of paper.

The three following species are very similar to this in character of wood and are of practically identical paper-making value.

Aspen (Populus tremuloides). Ranges from southern Labrador to Hudson Bay and northwestward to the Mackenzie River and Alaska; southward to Pennsylvania, northeastern Missouri, southern Nebraska, and throughout the western mountains to northern New Mexico and Arizona and central California.

Balsam Poplar (Populus balsamifera). Ranges from the coast of Alaska and the valley of the Mackenzie River to Hudson Bay and Newfoundland; southward to northern New England and New York, central Michigan and Minnesota, northwestern Nebraska, northern Montana, Idaho, Oregon, and Nevada.

Cottonwood (Populus deltoides). Ranges from Quebec and Vermont through western New England and New York, Pennsylvania, Maryland, and Atlantic States to western Florida and west to the Rocky Mountains.

White Birch — Gray Birch (Betula populifolia). Ranges from Nova Scotia, New Brunswick, and lower St. Lawrence River southward

to Delaware and westward through northern New England and New York to Lake Ontario.

The wood is light, soft, not strong, close grained, not durable; color light brown with thick, nearly white sapwood.

This wood is easily reduced to pulp by the soda process, and the fiber bleaches readily. The chief difficulty in its use is in the economical removal of the bark.

Paper Birch (Betula papyrifera). Ranges from Labrador to Hudson Bay, Great Bear Lake, Yukon River, and coast of Alaska; southward to New York, northern Pennsylvania, central Michigan and Minnesota, northern Nebraska, Dakota, northern Montana, and northwestern Washington.

The wood is light, strong, hard, tough, and close grained; its color is light brown tinged with red, and the sapwood is nearly white. The bark is removed from this wood with some difficulty and as even the inner bark causes dirt in the pulp it must be very completely removed.

Paper birch cooks by the soda process with a little more difficulty than poplar, and the fiber requires slightly more bleach. It yields pulp similar to poplar and fully equal to it in quality. It also cooks readily by the sulfite process, and the fiber bleaches to a very high white.

Yellow Birch (Betula lutea). Ranges from Newfoundland and along the northern shores of St. Lawrence Gulf to Abittibi Lake and Rainy River; southward to northern Minnesota and through the northern states to eastern Tennessee, North Carolina, and Delaware.

The wood is heavy, straight grained, and reddish brown in color.

This birch also cooks easily by the soda process and gives fiber which is superior to that from aspen in strength characteristics, though rather harder to bleach.

Red Alder (Alnus rubra). Ranges from Sitka through the coast ranges of British Columbia, Washington, and Oregon to California.

The wood is light, brittle, fine grained; color, pale reddish brown.

This wood cooks readily by the soda process, yielding a fiber very similar to poplar.

Beech (Fagus grandifolia). Ranges from Nova Scotia to Lake Huron and northern Wisconsin; south to western Florida and west to southeastern Missouri and Texas.

The wood is very hard, strong, tough, very close grained, not durable in contact with soil, inclined to check on drying; color, dark or light red with nearly white sapwood.

Beech cooked by the soda process requires a little more severe treatment than poplar. The pulp is soft and easily bleached, though not quite so easily as poplar.

Chestnut (Castanea dentata). Ranges from southern Maine to northwestern Vermont, southern Ontario and the southern shores of Lake Ontario to southeastern Michigan; southward to Delaware and southeastern Indiana and on the Allegheny Mountains to central Kentucky and Tennessee, central Alabama, and Mississippi.

The wood is light, soft, not strong, coarse grained, liable to check and warp in drying, easily split, very durable in contact with soil. It is reddish brown in color.

Chestnut wood contains tannin, which can be profitably extracted for use in tanning or other industries. The extracted chips cook quite readily by the soda process, and the fiber bleaches without much difficulty. If the tannin is not removed the fiber is hard to bleach. Chestnut fiber is short and is used as a substitute for poplar.

The blight has killed most of the chestnut trees in the Appalachian region but the dead wood is still being used for tannin and pulp making, more especially by the semi-chemical process for boards.

Cucumber Magnolia (Magnolia acuminata). Ranges from western New York through southern Ontario to Illinois and south in the Appalachian Mountains to southern Alabama and northeastern Mississippi; central Kentucky and Tennessee.

The wood is soft, light, not strong, close grained, and easily worked; color, light yellow with nearly white sapwood.

This wood reduces easily by the soda process, giving a fiber closely resembling poplar in its paper-making value.

Yellow Poplar (Liriodendron tulipifera). Ranges from Rhode Island to southwestern Vermont and west to Lake Michigan; south to Florida, southern Alabama, and Mississippi.

The wood is light, soft, brittle, not strong, easily worked; its color is light yellow or brown with creamy white sapwood.

Yellow poplar is readily reduced by the soda process, yielding a fiber which is similar to poplar though generally a trifle longer.

Red Gum (Liquidamber styraciflua). Ranges from Connecticut to southeastern Missouri and Arkansas; south to Florida and Texas.

The wood is heavy, hard, not strong, straight and close grained, inclined to shrink and warp badly in seasoning. Color, bright brown tinged with red; sapwood, nearly white.

Red gum can be treated by the chemical processes about as easily as poplar; the fiber is considerably longer than poplar but not long enough to bring it into the class with spruce and other coniferous woods.

Black Gum (Nyssa sylvatica). Ranges from Maine to Florida and west to southern Ontario, southern Michigan, southeastern Missouri, and Texas.

The wood is heavy, soft, strong, fine grained, very difficult to split; in color it is light yellow or nearly white.

By the soda process it cooks nearly as easily as poplar and yields a fiber which bleaches a little harder than poplar pulp. Its fiber is longer than that from poplar and makes excellent paper. A very white groundwood may be made from freshly cut or rapidly dried black gum wood. The pulp is not strong and is not entirely suitable for newsprint but it finds a use in certain specialties.

Sycamore (Platanus occidentalis). Ranges from southeastern New Hampshire and southern Maine to northern Vermont and Lake Ontario; west to eastern Nebraska and Kansas, and south to northern Florida, central Alabama, Mississippi, and Texas.

The wood is rather light, hard, coarse grained, not very strong, very hard to split.

Sycamore cooks easily by the soda process, and the fiber is longer and more slender than that from poplar; it is said, however, to give a rather " punky " paper.

Sugar Maple, Hard Maple (Acer saccharum). Ranges from southern Newfoundland to Lake of the Woods and Minnesota; south to northern Georgia and western Florida; west to eastern Nebraska, Kansas, and Texas.

The wood is heavy, hard, strong, tough, and close grained; in color it is light brown tinged with red.

By the soda process it is reduced about as easily as poplar; the fiber is shorter than poplar but bleaches readily.

Silver Maple, White Maple (Acer saccharinum). Ranges from New Brunswick to western Florida; west to southern Ontario, through Michigan to eastern Dakota, Nebraska, and Kansas.

The wood is moderately light, hard, strong, close grained, easily worked but rather brittle.

It is reduced by the soda process as readily as poplar and makes a paper of practically the same quality. The fiber is a little shorter than poplar and bleaches readily.

Red Maple (Acer rubrum). Ranges from New Brunswick, Quebec, and Ontario to Florida; west to Lake of the Woods, eastern Dakota, Nebraska, and Texas.

The wood is very heavy, close grained, not strong; its color is light brown slightly tinged with red, the thick sapwood is lighter colored.

Red maple is slightly more difficult to treat than poplar; the fiber is rather shorter than poplar and bleaches a little harder.

Basswood (*Tilia glabra*). Ranges from New Brunswick to Virginia, Georgia, and Alabama; west to Lake Superior, Lake Winnipeg, eastern Dakota, Nebraska, Kansas, and Texas.

The wood is light, soft, not strong, very close grained, compact and easily worked; color, light brown tinged with red.

It is very easily reduced by the soda process and yields an easy bleaching pulp very similar to poplar.

BULK OF RAW MATERIALS

This is an important factor to be considered in the transportation, storage and cooking of the different materials, yet very few figures have apparently been published. The following notes therefore make no claim to completeness but are merely an attempt to collect in one place what little information is available.

Rags. Bales of rags as received at the mill have been found to have the following weights:

	LB. PER CU. FT.
Egyptian rags	37.5
Blue cottons	26.5
White cottons	19.5–22.1

When dusted and dumped into bins, but not tamped, they weigh 15.6 lb. per cu. ft. before cutting.

Straw. Weighings of rice straw gave the following results:

	LB. PER CU. FT.
As baled for shipment	11.
Chopped and tamped	4.7
Chopped and not tamped	3.3

Esparto. Beadle and Stevens[1] give the figures for esparto as 120 cu. ft. per ton when pressed as usual or 90 cu. ft. from hydraulic presses.

A boiler of 540-cu.-ft. capacity (vomiting type) will hold 50 cwt. of esparto, which after cooking will occupy a volume of 300 cu. ft.

Wood. The number of cubic feet of solid wood per cord and the consequent weight per cord vary greatly with the kinds of wood, the size of the logs, their form, whether crooked or straight, and the dimensions of the cord as piled. Graves[3] gives the data in Table 7 for the number of solid cubic feet for sticks of various diameters. These figures are apparently for cords of 128 cu. ft. stacked volume of barked logs.

TABLE 7

Diameter of Sticks	No. of Sticks per Cord	Solid Cubic Feet per Cord of		
		Hardwoods	Softwoods	Mixed
In.				
6.8	94	102.40	102.40	102.40
6.0	126	94.72	98.56	96.00
4.75	205	88.32	97.28	92.16
3.5	378	79.36	90.88	84.48

Table 8 is compiled from data supplied by the Forest Products Laboratory. The figures do not represent average conditions, but merely some of the shipments received at the laboratory.

TABLE 8

Wood	Weight per Cord		Solid Wood Volume of Cord	Sticks per Cord	Diameter of Barked Logs		
	Unbarked as Received	Barked Oven-Dry			Max.	Min.	Av.
	Lb.		Cu. Ft.		In.	In.	In.
White spruce...	4570	2170	86.2	49	10.4	8.2	9.2
Lowland fir....	5195	2155	84.5	71	15.0	4.8	10.7
Hemlock, eastern.........	5087	1960	77.7	106	8.3	4.0	5.8
western.....	5190	2411	89.2	32	16.5	8.3	11.5
Pine, jack.....	4820	2032	82.0	73	8.4	5.3	6.8
longleaf......	6374	2920	82.3	89	7.6	5.4	6.5
slash........	5577	2440	75.8	109	8.3	3.0	5.6
loblolly......	5500	2550	80.2	73	9.6	4.8	7.1
White birch...	5680	2820	88.1	68	11.1	5.3	7.6
Aspen.........	4607	2065	78.2	77	10.6	4.4	7.0
Sugar maple ..	5720	2840	78.5	62	10.9	5.2	7.2
Black gum.....	5677	2620	76.2	67	12.5	4.2	7.1

Measurements by the author on carefully stacked, peeled poplar wood in 4-ft. lengths show in Table 9 the variation in weight per cord with the size of the sticks.

Wells and Rue[33] make the following statement: " Rossed 2-ft. spruce bolts of mixed diameters ranging from 6 to 14 in. contain slightly over 100 cu. ft. per cord.   Four-foot rossed bolts run 2 to 3 per cent less, 4-ft. peeled bolts about 7 per cent less, and 4-ft. rough bolts from 20 to 25 per cent less.   The solid cubical contents of mill waste varies enormously.   Frequently 2 cords of mill waste will be found to yield only

TABLE 9

Average Diameter of Sticks	No. of Sticks per Cord	Weight per Cord, Air Dry	Per Cent Moisture	Weight per Cord, Bone Dry
In.		Lb.		Lb.
11.72	35.5	4295	34.2	2828
7.90	70.5	3610	29.3	2553
3.18	....	2625	19.7	2108

as much solid wood as 1 cord of 4-ft. round bolts with the bark on."

Sound poplar wood when chipped, blown into a bin, and leveled off but not tamped, occupied a space of 259 cu. ft. per cord of wood for an average of three tests. The chips, when placed loosely into a measuring box, weighed 10.8 lb. per cu. ft. and if thoroughly shaken down but not tamped 13.8 lb. per cu. ft.

Spruce wood gave, in one test, the following figures:

One cord air-dry spruce with bark weighs .... 4500 lb.
Same after disk barking weighs .... 3600 lb.
Volume of chips from above is .... 260 cu. ft.
One cubic foot of chips weighs .... 13 lb.

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CHAPTER III

RAGS AND NON-WOODY MATERIALS

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Rags. Before the development of mechanical and chemical processes for making wood pulp, rag fibers were the chief source of raw materials for paper making, but more recently they have been displaced by sulfite and sulfate fibers, and more especially the purified wood fibers, until now they are seldom used except in roofing papers, fiber boards, blottings, and the highest grades of writing papers.

In 1929 the Census Bureau reported 739,422 tons of rags used in the paper industry, and of this total the Writing Paper Manufacturers Association estimated that 58,000 tons were used in fine papers and the balance in the other grades mentioned. Of these rags about 70 per cent were domestic and the rest imported; in 1937 about 82 per cent were from domestic sources.

The tendency to substitute wood fibers for rags is pointed out by Dobrow,[14] who states that in 1914 only 30 per cent of the writing papers were made from sulfite, while in 1935 this figure had risen to 83 per cent. There is still, however, a field for high-quality, rag-content papers, where durability, permanence, appearance, and prestige are important factors.

The two main sources of supply for rags are new cuttings from the textile and garment factories, and old rags collected from households. The grades of rags differ from time to time depending somewhat upon the prevailing fashions. Among those currently listed are the following:

New Rags

No. 1 white linens	Unbleached hosiery
No. 1 gray linens	Bleached hosiery
Blue linens	White drill cuttings
No. 1 white shirt cuttings	No. 1 washables
No. 1 unbleached muslins	Tire threads
No. 1 unbleached shoe cuttings	Canton flannel and glove cuttings
No. 1 light sleeve linings (silesias)	Ticking and mattress
No. 1 light prints or percales	No. 2 unbleached muslins
No. 1 fancy shirt cuttings	No. 2 unbleached shoe cuttings
No. 1 white back blue overall cuttings	Light striped pants cuttings
No. 1 light flannelettes	Blue Cheviots

OLD RAGS

No. 1 white linens	Thirds and blues, miscl.
No. 1 old whites	Blue overalls
Extra thirds and blues	Twos and blues

The grade of rags to use depends on the quality of paper to be made. For writing papers the fiber should have good color, strength, and durability, with a high alpha-cellulose content. New white cuttings and new unbleached rags yield such fiber with a minimum of chemical treatment. Carefully controlled rag stock bleaching is less severe than the usual textile bleaching, so unbleached cuttings, such as muslins, can be made into fiber equal in color to that from the new bleached cuttings and of greater strength than that from textile fibers.

Colored rags must be carefully selected for bleachability. Some contain only one dye, while others contain many different types, and since the demand in fabrics is for greater color fastness and resistance to washing, the problem of removing the colors is becoming more complicated and difficult. In many cases color cannot be removed, and with some cuttings containing several dyes, some colors are removed while others are unaffected. For this reason many grades of new rags cannot be used in white papers. Occasionally some colored cuttings give a pulp of a shade which can be used in certain colored papers, but it is not general practice to handle unbleachable cuttings in this way.

In recent years some of the new synthetic fibers have been blended with staple cotton in certain fabrics. As with wool-cotton mixtures, the presence of synthetic fibers usually results in unduly high shrinkages in the pulping operation, or it may cause serious trouble in subsequent paper-making operations. Cellulose acetate either as fibers or as a sizing agent has been known to cause considerable trouble. Acetate fibers may be identified readily by treating the cuttings for 5 minutes at 150° to 160° F. with a solution of 0.2 gram per liter of Celanthrene Violet C. B. Powder, which has no affinity for cotton, but dyes acetate fibers readily.[15] It is best to include a piece of cotton material for comparison.

Very fine strands of rubber are sometimes present in cuttings, especially in knit goods, and it is often difficult to detect this material except by very careful inspection. Rubber compounds are also used for special treatment of textiles, and cuttings containing such materials should be avoided.

Textile cuttings often contain special sizing agents which are used to facilitate spinning and weaving, and also to impart certain properties such as water repellency or wrinkle proofing to the finished goods. A great many materials have been used, and new products are continually

appearing. Many of these cannot be removed in pulping operations, since they tend to agglomerate and form specks in the final product. Others are hydrolyzed or saponified in the alkaline boil, and some can be emulsified and removed. The newer types of wetting-out agents, such as the sulfonated higher alcohols, are said to be useful in this connection, but there is some doubt whether they are of sufficient value to warrant their use.

Preparing the Rags. The first step in preparing rags is generally a dusting or thrashing. This is not required by new, clean textile cuttings, but is necessary for old rags in order to remove dirt in the creases and seams. The bales are opened and the loosened rags thrown into a thrasher, which is usually a rapidly revolving cylinder covered with teeth or spikes, enclosed in an outer cylindrical casing, also fitted with teeth. After this dusting the rags are sorted into the various arbitrary grades maintained at the mill in question. The second grading is desirable because the sorting before baling is frequently imperfect, leaving at times from 10 to 45 per cent of off-grade rags. During this sorting the larger rags are cut into pieces, the seams are opened, and buckles, buttons, hooks, iron, etc., removed. Skill and judgment are required to sort and grade rags correctly, and much of the success of subsequent operations depends on the care with which it is done. New rag cuttings are also carefully examined and pieces of wood, colored paper, jute, string, and unbleachable material are removed.

The next step is cutting the sorted rags into pieces 2 to 4 inches square. This is generally done by machinery, although hand cutting is sometimes practiced. Machine cutting causes greater waste in the form of dust and bits of rag, and the rags are more stringy and do not empty from the rotary as quickly as hand-cut rags, but if the cutter knives are sharpened frequently these disadvantages are not serious. After cutting, the rags are given a final dusting in some form of "willow," which permits the dust to pass through the wire covering while the clean rags are delivered into cars or conveyed mechanically to the boilers. Sometimes the dusted rags are passed over a magnetic separator to take out bits of iron and steel which escaped the sorters. These include hooks and eyes, metal clasps, tacks, nails, buttons, needles, etc.

Cooking the Rags. The object of the boiling process is to dissolve or saponify the grease, loosen the dirt and other impurities so that they may be easily washed out, and destroy or so modify the coloring matters that they may be readily bleached. Another important function is to destroy wool which may have escaped the sorting operation. The agents for effecting these changes are caustic lime, caustic soda,

or a mixture of lime and soda ash. The question of which to choose depends largely on personal preference and on the type of boiler used.
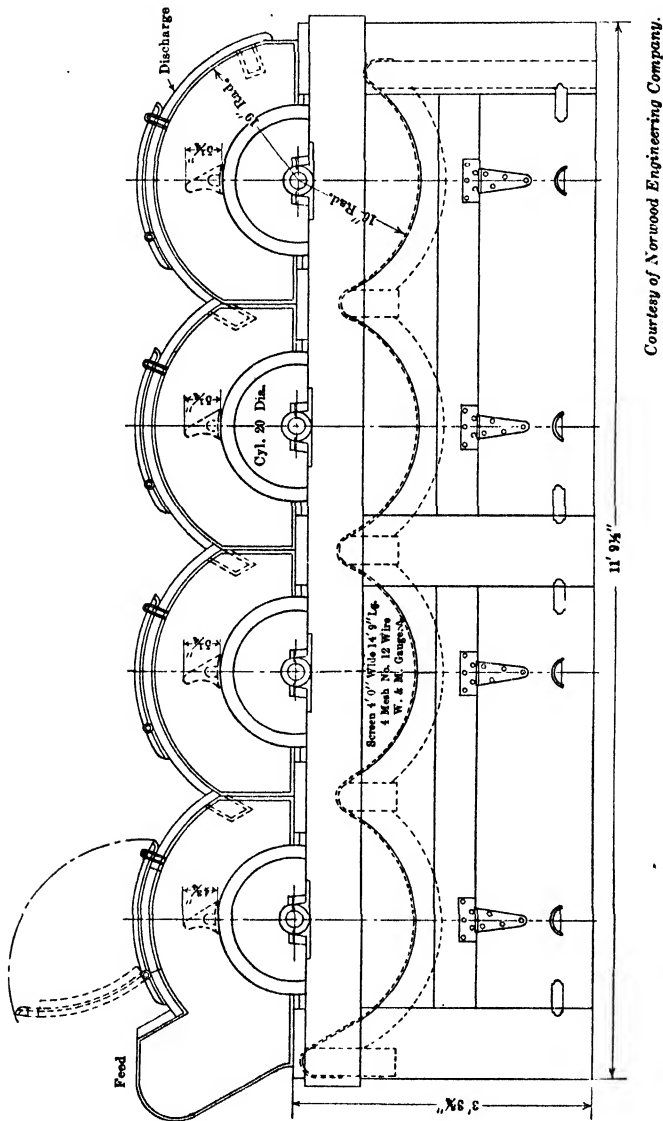
FIG. 12.   RAILROAD RAG DUSTER.

Lime is only slightly soluble in water, 1 part dissolving in 1500 parts of water at 212° F., or in 728 parts at 68° F. It forms insoluble compounds with the grease and other impurities in the rags and is

thus removed from solution, but a fresh portion dissolves to take its place, so that the concentration of alkali is practically constant throughout the boil. The slight solubility of the lime limits the speed of reaction, and the only way to make up for it is to increase the time of treatment. On the other hand it prevents injury to the fiber from too great concentration of alkali, and is therefore more likely to give good results when the common unscientific methods of control are used.

Caustic soda acts in the same way as lime but is readily soluble in water and the compounds formed also remain in solution and are more easily washed out. Because of its solubility the rags are first subjected to strong solutions which continually diminish in strength as the treatment continues. If the caustic soda is the chemical equivalent of the lime generally employed, the rags will probably be overcooked and tender and the yield low, but if smaller amounts are used and the time of boiling properly regulated there is no reason to think that it will give inferior fiber or a lower yield than a lime cook on the same stock. Lime-boiled rags are brighter in color than those boiled with caustic soda, but this difference frequently disappears after bleaching. The rapidity with which the alkali is used up in a soda boil is shown in the following condensed data from large-scale experiments by Beadle:[2]

Rags	Gals per Cwt.	Liquor Per Cent Na_2O	Per Cent Na_2O on Rags	Free Na_2O at Hours below, start being 100%				
				1	2	3	4	5
1 and 2 cottons	24	0.33	0.697	38	15	8	..	..
2nd cottons	25.7	0.654	1.68	48	24	19	..	..
3rd cottons	22–22.5	0.55–0.90	1.22–1.78	31–70	21–43	13–26	10–23	..
Linens	23–25	0.91–1.36	1.91–2.45	25–80	16–24	9–19	7–13	0–13

Similar experiments by Bialkowsky on 5-ton cooks of new blue denims using caustic soda showed the following results:

Gals per Cwt.	Liquor Per Cent Na_2O	Free Na_2O at Hours below, start being 100%			
		1½	3	4	5
29	0.96	53	49	42	36
29	0.64	61	35	..	16

The severity of the treatment given rags varies in different mills, with the grade of rags and with the kind of paper made. The caustic

soda necessary is variously given as from 1 to 10 per cent, and the lime from 5 to 20 per cent of the weight of the rags. The steam pressure runs from 11 to 50 pounds, 30 pounds being a fair average; the time of boiling ranges from 2 to 14 hours and has been as long as 30 hours. Lime necessitates longer cooks than soda, but the tendency is toward the shorter cooks to save steam and increase the yields and the capacity of the plant. Watt[39] gives the European practice as 12 hours at 30 pounds pressure, using 216 to 378 pounds of lime and 114 to 190 pounds of 48 per cent soda ash for 4000 pounds of rags. In general dark-colored or very dirty rags require much more severe treatment than new cuttings or clean, light-colored stock.

Starch in new cuttings is said to interfere with the boiling by gelatinizing and preventing penetration of the alkali. This probably takes place very seldom, but if it does it can be overcome by heating the rags with water to about 160° F. and adding diastase or some of the modern enzymes. In a short time the starch will be hydrolyzed and the cook may be finished with alkali as usual.
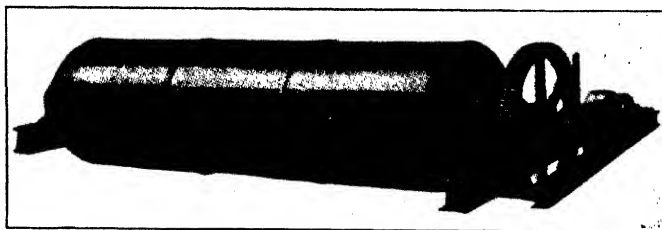
Courtesy Biggs Boiler Works Company.

FIG. 13.   ROTARY RAG BOILER.

The lime used for rag cooking should slake rapidly and completely and be as free as possible from iron. It is generally conceded that its value for this work is in proportion to its content of available CaO, and little attention seems to be paid to the small amounts of impurities other than iron. The volume of lime milk to add to a rotary boiler is generally that which will fill it from one-half to two-thirds full after the rags are in. If they are not covered, but are exposed to the steam, they may become tender and brittle.

Several types of boilers are used for cooking rags; spherical or cylindrical rotary boilers, and stationary boilers in which the circulation of the liquor is maintained either by a pump or by a vomiting pipe connected with a false bottom. In the last, the steam enters under the false bottom and in passing up the pipe carries along the cooking liquor, which is then distributed over the charge by baffle plates. Both types

of boiler are fitted with safety valves or some means of preventing the line pressure exceeding a predetermined value. It is claimed that stationary boilers cause less loss because the rags are not in motion and there is no rubbing off of the weaker fibers. On the other hand they require more steam, are not suitable for use with lime cooks, and take longer to discharge, since the cooked rags must all be removed by hand through manholes. Stationary boilers are largely used in Great Britain but almost never in this country. Of the rotary boilers the cylindrical is more generally employed than the spherical, though the shape of the latter helps greatly in discharging the contents.

The boilers are charged through manholes, and the men frequently enter the larger ones in order to pack the rags properly. The steam enters through the trunnions and passes through gratings on the inside and then into the charge. They are also fitted with strainers through which much dirt passes when blowing off pressure. Rotaries usually turn at a speed of 1 revolution in 2 to 5 minutes. The consequent agitation and friction of the rags loosen the lime compounds formed and allow the action to continue on the remaining fatty materials. When the cook is completed the liquor and steam are blown off through the strainers and blow-off cocks, the manhole covers are removed, and the contents are discharged by allowing the boiler to revolve; even a large cylindrical boiler will empty itself clean in this way. With competent labor such a boiler holding 5000 to 5200 pounds of rags requires $1\frac{1}{2}$ hours for charging. 2 hours for blowing off the liquor, and 3 hours for discharging the rags.

During the cooking of rags a small amount of ammonia is given off, tests on a large scale showing the following:

	Per Cent NH_3
From Japanese blues	0.22
From second white stock	0.05
From clean white linens	0.14
From German blues	0.33

Strong reducing agents such as zinc dust, titanium tetrachloride, alkaline sulfides, formaldehyde-sulfoxalates, and hydrosulfites can be used to decolorize certain dyes or to convert them to a soluble form. Sodium hydrosulfite strips the color from rags dyed with indigo and the azo colors of the direct acid and basic classes. It does not strip rags dyed with vat colors other than indigo, but lightens the color of rags dyed with sulfur colors.[22]

Lehner[23] recommends the following treatment for removing indigo from rags. Cook with 6 per cent of lime and 3 per cent of soda ash, or

with 3.5 per cent of caustic soda, for 3.5 hours at 40 pounds pressure, blow down, and refill with warm water. Entrance of air must be avoided by keeping the manhole covers on and making all fillings and emptyings, except the first, through connections with the blow-off valve. Turn on steam, roll the rotary half an hour, and blow down to remove coloring matter loosened by the alkaline cooking. Run in a solution containing 0.75 per cent sodium hydrosulfite and 0.5 per cent of soda ash on the dry weight of the rags, heat to 90–100° C., and roll for 2 hours. Blow down and repeat the treatment, using 0.5 per cent of each chemical the second time. Dump the rags from the rotary and wash as usual.

This process gives stock of good strength and color but involves too many fillings and emptyings of the rotary. Many mills have obtained good results with a two-stage alkaline cook, using hydrosulfite in both stages, the total amount being about 1 to 1.5 per cent on the weight of the rags.

Washing the cooked rags is usually done in large engines similar to beaters. One or more cylinder washers covered with perforated metal or wire cloth, frequently old Fourdrinier wire, serve to remove the dirty water, which is constantly replaced by fresh. If the rags stand some time with the lime on them before washing they are softer, more absorbent, and better for blotting papers; immediate washing gives harder stock of better color. The lime compounds formed during cooking are friable and in general easily washed out, but occasionally enough mineral oil is present to cause sticky masses of dirt to collect on the sides of the beater, fill up the openings of the washing drums, and appear as small globules in the rag stock itself. When lime is used the washing should always be done with cold water because of the greater solubility of lime at low temperatures.

When the water leaving the cylinder washers is fairly clear the beater roll is lowered to reduce the rags to half stuff and loosen up the remaining dirt. If this is done too soon the fiber loss is unduly great, the frayed-out fibers catch the dirt, and the resulting stock is of poor color. After the rags are reduced to half stuff the bleach is added and the charge put into drainers, where bleaching is completed and the stock washed, dewatered, and stored.

The amount of water used in preparing rag stock is very considerable. Sindall[38] states that to wash the rag stock for a ton of paper requires 25,000 and 35,000 gallons. Beadle[3] estimates the quantity in Imperial gallons used in preparing the rags for a ton of two grades of paper to be as follows:

	BANK PAPER	RAG PAPER
Boiling the rags	1,500	1,100
Rinsing	1,500	....
Washing in engines	40,000	37,830
Washing out bleach	5,000	5,000
	48,000	43,930

Extensive tests made at an American mill making high-grade writing papers indicate a water consumption of 80,000 to 100,000 gallons per ton of pulp.

The rate of removal of lime and dirt during washing is shown in Table 10, which gives the average of many tests on 1000-pound washers with a flow of 10,000 gallons per hour per washer.

TABLE 10

Washing Time	Suspended Solids	Lime
	Grams per liter	Grams per liter
Start	4.0	2.32
15 minutes	0.63	....
30 minutes	0.32	0.37
45 minutes	0.16	....
1 hour	0.08	0.098
2 hours	0.04	0.018
3 hours	0.04	0.012
4 hours	0.04	0.005

In general from 80 to 90 per cent of the residual chemicals and dirt is removed in the first hour of washing; after that the amount removed per hour is nearly constant. The time of washing should be so adjusted as to give maximum cleanliness with minimum fiber loss; this will require 4 to 6 hours, with as much as 14 hours in extreme cases. With linens, white shirt cuttings, hosiery, etc., the treatment is determined by the time necessary to draw out the fibers and undo the work of the spinner and weaver. Eight to twelve hours covers the range in this class.

The losses which rags undergo in making into paper vary enormously with the quality of the rags and the treatment given. Table 11, condensed from data in Hofmann's " Papier Fabrikation," shows the losses in preparing half stuff from different materials.

TABLE 11

Kind of Material	Moisture	Cutting and Dusting	Cooking and Washing	Beating into Half Stuff	Bleaching	Total Loss	Bone-Dry Half Stuff from 100 Kg. Rags
	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Kg.
White linens............	5-7	4-5	7-12	4-9	3-6	26-33	67-74
Bagging................	5-11	5-7	11-18	12-14	5-9	42-55	45-58
White cotton	4-5	5	11-13	8-9	4	34	66
Red and white calico	6	6	12-13	12-13	4-5	40-42	58-60
Half wool and old rags...	6	6	38	10	4	64	36
Blue linen	6-7	6	10-13	9-14	4-5	35-45	55-65

Similar data from an American book paper mill using rotary boilers are shown in Table 12.

TABLE 12

Kind of Material	Sorting and Tare	Thrashing	Cutting	Total Loss to Finished Paper
	Per cent	Per cent	Per cent	
Japanese blues..........	3.1	2.4	3.6	34.6
New calico..............	5.9	4.0	0.4	26.2
Belgian blues...........	3.5	4.9	2.8	42.2
Whites.................	1.5	0.2	5.0	25.5
Muslins................	7.8	1.8	3.1	41.7
Russian blue linen.......	3.7	2.5	6.7	45.8

Beadle[4] gives the following losses for English practice:

	BOILING	BLEACHING
New cotton (best grade)	8.71	3.29
Low grade cottons	12.20	7.70
No. 1 cotton rags	5.80	6.20
No. 3 cotton rags	12.50	4.30
New unbleached cottons	23.50	13.00

To produce stock of maximum durability and permanence great care must be taken in cooking, and especially in bleaching, and the experience of the textile mills and knowledge of the chemical and physical changes taking place in the cotton fiber during the various treatments can be applied to advantage. In general the alkaline cook removes soluble cellulose constituents, and if conditions of alkali concentration, time, temperature, and pressure are too severe, continued degradation occurs throughout the cook. Laughlin[21] found that pressures above 150 pounds were not suitable in commercial rag cooking because of ex-

cessive degradation. Pressures up to 100 or 150 pounds are not particularly degrading if the cook does not exceed 3 hours, with a concentration of not over $3\frac{1}{2}$ per cent of sodium hydroxide or 10 per cent of lime on the weight of rags. The stability of the fibers, as measured by viscosity and tearing strength, is much less affected by the time of cooking than by pressure and chemical concentration. Cooking losses are small if the concentration does not exceed 3 per cent sodium hydroxide, or the pressure 100 pounds, but in excess of these conditions losses increase rapidly.

The usual bleaching agent for rag stock is calcium hypochlorite, though other agents such as perborate, peroxide, permanganate, and gaseous chlorine have been suggested. Sulfuric acid or alum is sometimes added during bleaching to speed up the reaction. Clibbens and Ridge[11] made a comprehensive study of the chemical modification of cellulose during hypochlorite bleaching and found that at the neutral point the degradation was faster than in either acid or alkaline solution. This was shown by copper number, methylene blue absorption, and viscosity in cuprammonium. Bialkowsky[5] also found that the cuprammonium viscosity was lowered by cooking and bleaching, but not much affected by beating; within certain limits the folding endurance of the finished paper decreased with decrease in viscosity.

Crain[12] investigated the variables in bleaching rag stock with calcium hypochlorite and under ordinary conditions found the loss in weight to be only 0.2 to 0.4 per cent. The rate of degradation was dependent upon the concentration of the bleach solution and, within limits, independent of the ratio of available chlorine to stock. The extent of degradation was related to the time of treatment, though the rate of degradation fell as the time of treatment was prolonged. As the temperature of bleaching rose the rate of degradation increased, and above 45° C. the change in the cellulose was very rapid. Within a pH range of 4.5 to 10.0 the most rapid degradation occurred at about 6.8.

Cottonseed Linters and Hull Fiber. Cotton as picked in the fields is first ginned to remove fiber suitable for spinning, and the seed is then put through a "linter" machine which resembles a gin except for the closer saw settings. This removes either 20 to 40 pounds of fiber per ton of seed as first-cut linters, or 90 to 160 pounds as mill-run linters. If the former is produced, the seed passes through a second machine which takes a closer cut of fiber; from 80 to 90 pounds of this second-cut linters is ordinarily obtained. The seed next goes through machines which split the seed coat and remove the kernels for oil and cake. The split hulls are then ground in hammer mills

and the remaining hull fibers separated from the bran by mechanical means.

Of these four fiber types, three are converted into cellulose pulps for the chemical cellulose industry; the first-cut linters, and to a certain extent mill-run linters, are not used for this purpose because of their greater value as spinning fibers or as batting. A small percentage of the types used for chemical cellulose is utilized for paper making.

The equipment for converting linters and hull fiber into chemical cellulose is somewhat similar to that used in the wood pulp soda process. Cooking is carried out in vertical stationary digesters, employing a 1.5 to 3.0 per cent caustic soda solution containing 0.1 to 0.3 per cent of a soap-forming substance for detergent purposes. The cook is conducted at 30 to 105 pounds pressure for 2 to 6 hours, and after the digester is discharged by blowing, the pulp is washed and bleached.

Bleaching is best done in a multistage process, after the manner of sulfite wood pulp except for the employment of much lower bleach concentrations because of the lower bleach requirement of cottonseed pulps. After a final washing the pulp is dried, either in loose form in a tunnel dryer, after which it is baled, or in board form over a Fourdrinier machine. Most paper makers prefer the latter because it is free from the pilliness characteristic of cotton linters in the bulk dried state.

Munson[27] gives the yield of chemical cellulose from linters as 80 to 85 per cent, and the following as typical figures for the analyses of linters and chemical cotton.

	LINTERS PER CENT	CHEMICAL COTTON PER CENT
Ash	1.0–1.5	0.10
Iron	0.06	0.002
Ether extract	1.0	0.20
Lignin (H_2SO_4 method)	3.0	0.20
Moisture	6.0	5.0
Alpha-cellulose	..	99.0

For chemical cotton the cuprammonium viscosity is important and must be carefully controlled by proper adjustments in the chemical treatment. The temperature of digestion has a much greater influence on viscosity than time of cooking or chemical concentration. For low-viscosity pulps, cooking up to 80 pounds pressure or higher may be necessary. Medium- and high-viscosity types are produced by varying the time of treatment. Bleaching also tends to reduce the viscosity, the reduction depending on the severity of the process.

Cottonseed linters and hull fiber pulps find use in paper making chiefly because of their high purity. They are characterized by excellent color, by greater cleanliness than rag pulps, and by high alpha-cellulose content; their chief faults are that they are short, very free, and hard to hydrate. When such pulps must be hydrated it is best to use the longer-fibered grades, such as mill runs or long second cuts, but if hydration is not a factor the shorter second cuts and hull fibers are satisfactory. Approximately 1500 tons per year of these pulps are used in paper making.

Esparto.* Because of its cost esparto grass has never competed in this country with soda pulp prepared from wood, but in Europe, especially in Great Britain and France, it is one of the most important fibrous materials. It was introduced into England about 1860 by Routledge, and its use increased from 16 tons in 1861 to 184,000 tons in 1884. The present yearly consumption in Great Britain now amounts to about 300,000 tons.

Esparto is a reedy grass which grows wild in Spain and northern Africa, the quality varying considerably according to the locality of growth, the degree of ripening, and the care in harvesting. The Spanish variety, which is considered best, is brownish yellow in color. The north African varieties differ rather widely in quality, the best being almost equal to Spanish.

When mature the grass is plucked (not cut) by native labor, care being taken to avoid lifting the plant by its roots, and is then dried in the sun. When quite dry the grass is given a preliminary cleaning to remove useless material, and baled on site or after being transported to the coast. The average weight of a bale is about 200 pounds.

On arrival at the paper mill the bales of esparto are opened and passed through a willow or duster very similar to a rag duster, except that it is conical instead of cylindrical. On the under side of the casing is an open gridwork where suction is applied to extract the dust. The grass from the duster is conveyed to the digesters by means of belt carriers, or if the distance is appreciable, by air blast. In addition to sand and other mineral matter, the dust contains waxes. The fine dust, which has the highest wax content, is separated from the coarse grit and small pieces of grass, and constitutes a useful by-product. According to Beveridge[4] it contains about 29.2 per cent of mineral matter and 64.6 per cent of organic material (loss on ignition), of which about 90 per cent is waxy and greenish brown. The mineral matter contains silica, alumina, and calcium and magnesium carbon-

* Contributed by Dr. H. Ainsworth Harrison, F.I.C., chief chemist to Associated Paper Mills, Ltd., England.

ates. About 2 to $5\frac{1}{2}$ pounds of fine dust is obtained from 1 ton of
Spanish grass, and 5 to $7\frac{1}{2}$ pounds from Oran (Algerian). The col-
lected dust from most of the esparto mills in Great Britain is sent to a
mill in Scotland for solvent extraction of wax, which, because of its
hardness, is valuable in the manufacture of shoe and floor polishes.

Esparto grass is boiled in closed, stationary digesters very similar
to those described for rag cooking. The liquor is circulated by pumps
or vomiting pipes and distributed evenly over the upper surface of the
grass by a perforated dome placed about 12 inches below the top of
the chamber. Rotary boilers are not used as they cause the fibers to
roll up into small balls which are difficult to beat out and therefore
apt to form lumps in the paper. Digester capacities and conditions of
boiling vary from mill to mill, but average figures are as follows:

Capacity	2–5 tons of grass
Caustic soda	12–17 per cent
Time of boiling	2–5 hours
Steam pressure	30–60 lb. per sq. in.

The required quantity of liquor is run into the digester and steam
turned on. When the liquor begins to circulate, the grass is introduced
through an opening which passes through the perforated dome. As it
comes into contact with the stream of boiling liquor, it is softened and
can be packed more completely. Considerable skill is required at
this stage to insure even distribution of the grass; otherwise the liquor
will pass through any channels left and cause irregular cooking. It
takes about 45 minutes to fill a 5-ton digester. The time of cooking
varies inversely with the pressure and the strength of liquor employed.

Esparto requires much more caustic soda than rags; lime is never
used because it forms insoluble compounds. The amount of alkali
recommended by Dunbar for different grades of grass is as follows:

Fine Spanish	16.1–17.9 lb.	70 per cent caustic per 100 lb. grass								
Medium Spanish	14.3–16.1 "	"	"	"	"	"	"	"	"
Fine Oran	16.1 "	"	"	"	"	"	"	"	"
Medium Oran	14.3–15.2 "	"	"	"	"	"	"	"	"
Tripoli	17.0–17.9 "	"	"	"	"	"	"	"	"

The cooking liquor varies from $7°$ to $15°$ Tw. ($4.9°$ to $10.1°$ Bé.).

When cooking is complete the steam is blown off and the used liquor
run to the recovery plant. The boiled grass is then washed several
times with hot water to remove most of the spent liquor, each wash
going to the recovery plant. The pulpy mass is either dug out of the
boiler through a side door near the bottom or cut out by a high-pressure
water jet, and then goes to storage chests.

The boiling removes starches, lignins, and pectins. In some mills, where time permits, cooking is carried out in two stages, as recommended by Aitken.[1] The first boil is with a dilute solution containing 1.5 per cent caustic soda on the weight of grass. After an hour the liquor is drained off and replaced with 14 per cent by weight of caustic soda, and boiling is continued at 35–40 pounds pressure for about 3 hours. The liquor drawn off is pale amber in color; it may be diluted for a subsequent first boil or sent to the recovery system. This process is claimed to give greater economy in bleach and cleaner and more easily washed stock having a more permanent color.

Often the partially washed, cooked grass is pumped from the storage chest, through screens to remove unresolved clumps of grass, roots, and other foreign matter, to drum washers or potchers. More commonly, however, it is sent directly to the potchers for washing and bleaching. During washing a considerable quantity of short-fiber and cellular matter is lost.

The bleach consumption varies from 7 to 12 per cent (calculated as bleaching powder) of the unbleached fiber weight. The temperature is not allowed to exceed about 95° F.

When bleaching is complete, the stock is given a preliminary wash, then is greatly diluted and passed over sand tables to remove sand and grit; finally it goes to a press-pate which removes bleach residues and delivers it in a convenient condition for further operations. The yield of bleached fiber is about 42–45 per cent from Spanish grass and about 40 per cent for an average northern African variety. Tower bleaching has recently come into favor, as have also two- or three-stage processes.

Alkali is recovered from waste liquor in the same manner as that employed for black liquor from wood, using triple-effect evaporators and rotary furnaces. Under modern conditions a recovery of 90 per cent can be obtained.

Clark[10] describes the application of a Semi-Keebra process (75 per cent NaOH, 25 per cent Na_2SO_3) to esparto. This is stated to be a practical proposition and to give a stronger paper with more rattle than the usual types of esparto paper.

The special characteristics of esparto papers include pliability, ease of sizing, good opacity, excellent look-through, generous handle, and exceptionally fine printing qualities. Esparto paper also forms an ideal base for the production of high-quality coated papers.

Straw. Straw as used in paper making includes the stems and leaves of the various cereals, but wheat forms the chief supply. Much attention has been given to rice straw, and, except for its high silica content, there seems to be no technical reason why it could not be used as well

as other straws. Theoretically corn stalks should be included in this class of material, but structurally it more closely resembles bagasse; it is mentioned later.

The composition of straws varies greatly with the type of soil upon which they were grown. For this reason and because of the different methods used in analysis and interpreting results the available figures are difficult to compare, but from the results presented by several authors it is found that the ash content varies from 3.7 to 14.5 per cent of the bone-dry straw, and of this as much as 80 per cent may be silica. The most probable figures for cellulose (not pentosan-free) is from 46.5 to 53.5 per cent.[13] The silica content is of some importance if soda recovery is necessary, since much silica prevents satisfactory settling of the lime sludge in the usual causticizing process.

Straw is used for making two quite dissimilar products; a coarse, yellowish, halfstuff which is used for straw boards and cheap wrapping papers; and a bleached cellulose, similar to esparto in many of its properties, which is used in many high-grade products.

For making boards the straw is treated with lime milk for 8 to 10 hours at 35 to 45 pounds steam pressure, in rotary digesters which are usually globular and about 14 feet in diameter. In American practice the straw reaches the mill in bales which are stored in stacks near by; these stacks are often provided with roofs and sometimes with shelter on the sides. The straw deteriorates little, except on the very outside of the bales or at the bottom of the pile, and even that which has become very dark colored may be used by adding a little more lime to bring it to the right color. In filling the rotaries the bales are broken open and fed in without cutting, dusting, or any other preliminary operation; as much as a quarter of a bale is sometimes added without loosening up in any manner. As the rotary is filled, about a gallon of water is added for every $2\frac{1}{2}$ pounds of straw. The rotary is then revolved and steam admitted to raise the pressure to 25 pounds where it is held for about half an hour. The head is removed, more straw added, and the charge again steamed or " wilted " as before. This is repeated three or four times so that the final charge is about double that first added. At this point lime milk equivalent to about 10 per cent of CaO of the weight of the straw is added and the cook brought to pressure. Dolomitic lime is preferred to high-calcium lime if the cost is not too great; in this case the amount used is about 13 per cent. At the end of the cook the liquor is drained off under pressure; the charge is cooled until practically at atmospheric pressure and then dumped onto the floor, where it is seasoned for three to five days before use. The time required for one cook, including charging, cooking, and cooling, is about 24 hours.

The cooked straw is usually washed for about 4 hours in washing engines, the washing drum then raised, and beating proceeded with. The yield of board per ton of straw is generally figured as 1600 pounds for rye, 1400 pounds for wheat, and 1200 pounds for oat or rice. The washing removes excess lime and also much fiber, and the waste water from a 50-ton mill is claimed to be equivalent to the sewage from a city of 80,000 inhabitants. To avoid both the pollution problem and the loss of fiber Booth[6] proposed to use less lime in the digestion process and charge the hot, cooked straw into the beaters where it is easily defibered at the high temperature, and the digestion continues to some extent because of the residual chemicals. No washing is given, but as the stock is delivered to the paper machine the alkali is neutralized, one suitable reagent being chlorinated copperas, $Fe_2(SO_4)_3 \cdot FeCl_3$. If an excess of chlorine is used in making this it helps prevent decomposition in the straw pulp. Mills using this process report savings of 500 to 900 pounds of straw per ton of board made.

For making straw pulp for boards, Rue and Monsson[31] proposed cooking for 10 hours at 40 pounds gage pressure with $7\frac{1}{2}$ pounds of sodium carbonate and $1\frac{1}{4}$ pounds of sodium sulfite for 100 pounds of dry straw. The estimated cost is slightly more than for the lime process, but the product has less odor, less ash, and more cellulose, the yield is higher and the physical properties better.

Since 1928 many makers of corrugating paper have tended to use small amounts of caustic soda or soda ash with the lime in order to obtain stiffer products. The value of such papers does not justify the use of more than 3 per cent of soda. There has also been introduced[43] a process using 7 per cent of Na_2CO_3 and 1 per cent of sulfur, which is said to give superior corrugating paper.

Gibson[16] has proposed to utilize straw for insulating board by cooking at 60 to 70 pounds steam pressure for 8 hours with a relatively small amount of water and no alkali. The preparation of the stock is finished by mechanical disintegration.

Wells[41] states that lime is not very efficient in removing lignin, but that it neutralizes the acids formed during cooking and maintains alkaline conditions. It is more destructive to proteins than any of the other cooking agents. Lime-cooked pulp is soft and spongy while wet, but paper made from it dries to a hard, stiff sheet, noted for its ability to hold corrugations. Wet lime-cooked pulp parts with water more easily than other stocks, while soda-cooked straw pulp gives up water very slowly and dries to a harder, stiffer product.

High-grade bleached cellulose can be made from straw by any of the usual cooking procedures, and in Europe such products occupy an important place in the paper industry, though they are almost never

used in this country. The soda process is chiefly used, but of recent years a considerable amount of straw pulp has been made by the Pomilio soda-chlorine process.[28]*

Straw, being more highly lignified than esparto, requires a more drastic treatment; even the nodes must be so reduced that they will bleach readily. Because of this, and because of the loss of fine cells during the washing process, the yield from straw is less than that from esparto. Cross and Bevan[13] give the practical yield as about 35 per cent, while Beveridge[4] says that a mixture of equal parts of barley, oat, wheat, and rye straws will yield 40. to 41 per cent of air-dry, bleached cellulose.

In modern plants the straw is cut by rotary cutters into pieces 1 to 2 inches long, freed from dust, grain, etc., by an air blast, and fed into the boilers, steam and alkali being added at the same time to assist in packing the charge. Contrary to the practice with esparto, rotary boilers are preferred for straw because agitation permits a penetration of the liquor which cannot be obtained in a stationary cooker due to the close packing of the wet straw. The amount of alkali used varies greatly in different mills and with the kind of straw; it may be as low as 10 per cent or as high as 20 per cent of the weight of the straw. Experiments by the author on rice straw proved that a simple extraction with water at 20 to 25 pounds of steam pressure removed so much material that well-reduced and easily bleached fiber could be produced with 60 to 75 per cent of the caustic soda necessary for unextracted straw. Barley straw is said to require 20 per cent less soda than oat, wheat, or rye. The time of cooking is variously given as $3\frac{1}{2}$ to 8 hours, and the steam pressure as 10 to 90 pounds, with a decided tendency toward the use of the higher pressures of 70 to 90 pounds.

The cooked straw is run or blown from the boiler into wash tanks with false bottoms; these are preferred to drum washers because of the large loss of fine fibers and cellular matter which the latter cause. After washing, the straw is treated in edge-runners to crush the nodes and is then bleached in much the same way as esparto; the bleach required is from 7 to 10 per cent.

Recovery of alkali is carried out as in the soda process for wood or esparto, but is rendered difficult in many instances by the silica in the straw. This combines with the alkali, forming sodium silicate, and when the recovered ash is causticized the bulky, gelatinous precipitate of calcium silicate which forms prevents settling in the causticizing tanks and reduces the amount of soda which can be recovered.

* See Chapter VIII.

Beveridge[4] states that the soda lost varies with the amount of silica in the straw, the composition of the silicate formed, and the amount of potash rendered soluble from the ash constituents of the straw. He estimates that as much as 42 per cent of the total soda in the cooking liquor may be neutralized by the silica and claims that when the amount of silica in the straw approaches 3 to 4 per cent of its weight the recovered ash is of little value for further digestions.

Besides the soda and the Pomilio processes the sulfate process has been applied to straw with notable success. In isolated cases it is understood that good fiber has been prepared from straw by the sulfite process; apparently its large proportion of silica does not interfere in the treatment.

Straw cellulose makes a weaker paper than esparto, but it is suitable for mixing with rags or wood pulp for thin, hard, rattly papers. It tends to make the stock " wet " on the wire and imparts translucency to the papers in which it is used.

Flax Straw. Probably no member of the straw family, with the possible exception of corn stalks, has had so much study as flax straw. Large quantities are grown for seed production, and if a good quality of bast fiber could be prepared economically from the whole straw it would be of great assistance in supplying the demand for fibers for high-grade papers. Many of the more recent studies on flax straw, such as those of Bray and Peterson,[7, 8] and others,[32, 45, 34, 35, 36] take up the problem from the standpoint of the cooking reaction or the composition of the straw and give few data relating to the paper-making value of the product.

Schafer and Bray[33] give a brief general discussion of flax straw, production, composition, and value in the cellulose industries, and state that as received in bales it contains about 30 per cent of chaff, leaves, seed pods, weeds, and grasses. The bast fiber in the entire straw is about 15 to 20 per cent, and the woody fiber 70 to 75 per cent.

Studies by Wells and Schafer[44] indicate that the bast fiber and the shive, or woody portion of the stem, are widely different chemically. The bast fiber seems to consist of relatively pure cellulose with adsorbed carbohydrates which are soluble in hot water or in mild alkaline solutions, whereas the shive is composed of cellulose in close combination with lignin and pentosans. No way has yet been discovered of cooking the two together without overcooking the bast or undercooking the shive, either of which is fatal to the production of high-grade fiber. Tow prepared by mechanical separation of the bast from the shive can be made into good fiber, but with the machinery available it is impracticable to remove more than 75 per cent of the shive because

of the excessive loss of bast after a grade known as " fine tow " has been obtained. From studies made at the Bureau of Standards, Kellogg, Shaw, and Bicking[20] concluded that a fair grade of wrapper could be made from the whole straw, and a good quality of writing paper from tow if dirt specks were carefully eliminated. They found the consumption of chemicals high and the material not promising from a financial standpoint.

Bagasse and Corn Stalks. When straw is not available in sufficient amounts corn stalks are sometimes used with straw, or as a substitute for it, in making strawboard or corrugating paper.

Both bagasse and corn stalks are easily pulped by the alkaline processes, and the pulp gives a good color with less than 10 per cent of bleach. As the ash is considerably lower than in straw and contains much less silica, its effect on soda recovery is very slight. The chief obstacle to the use of these pulps is the presence of pith cells, and a two-stage cooking process has been proposed to get around this difficulty.[42] According to this the shredded corn stalks are first treated in a rod mill at a temperature of 93° C. with the partially spent liquor from the second stage. The unconsumed chemicals are quickly exhausted, and the material leaves the mill as slush pulp which can be washed by rotary filters or in any of the usual ways.

The pith and leaf cells are separated from the semi-cooked fibrous portion by flowing over inclined screens at low consistency. The cells are recovered by settling, while the fibrous portion is charged into digesters and cooked with enough caustic soda to complete the reduction and leave sufficient excess for the preliminary pulping. A digestion of 1¼ hours, with 15 minutes at 165° C., is sufficient. Four tons of corn stover will yield about a ton of pith material and a ton of bleached cellulose fiber. About 800 pounds of caustic soda are necessary for the double digestion.

Pulp made by this process is said to bleach to a high white color with 4 to 6 per cent of bleaching powder and to be soft and suitable for use alone or in mixed furnishes for making the better grades of writing and printing papers. The recovered pith cells may be used as part of the furnish for test liner, corrugating paper, chipboard, etc., and will increase the bursting strength of such products.

At least four attempts to use bagasse on a commercial basis have resulted in failure, chiefly because of the poor quality of the papers made. The history of the corn-stalk trials is not much better, and at present it seems fairly well proved that though good paper can be made from these materials it cannot be done economically in competition with wood.

Bamboo. Though not of immediate interest in this country, bamboo seems destined to hold an increasingly important place as a source of fiber because of its abundance and rapidity of growth and the high quality of the paper which it will make. According to Raitt,[29] in the Arakan Division of North Burma alone, there are over 16,000 square miles carrying a total crop of about 100,000,000 tons of bamboo. In Tenasserim in South Burma there are about 30,000,000 tons, and large crops are available in India, Siam, the Philippines, and Indo-China.

In the earlier attempts at pulping bamboo, culms of different ages were handled separately, nodes were not considered usable, alkali and bleach consumptions were high, and the yield of bleached pulp very low. Researches by Raitt and others have overcome most of these difficulties; the culms of all ages may be mixed, the nodes can be used after crushing, the alkali required has been reduced to 16 per cent and the bleach consumption to 8 per cent, and the bleached-pulp yield has been brought up to 42 per cent.

Analyses of typical Indian Bamboos reported by Raitt are given in Table 13, in which Group I, broadly classified by Raitt as starches, represents all neutral substances soluble in water at 100° C.; Group II, classified as pectins, includes materials insoluble in boiling water but soluble in 1 per cent NaOH solution at 100° C.; Group III includes lignins, or acid bodies soluble in 4 per cent NaOH solution at temperatures above 130° C. This table also gives the conditions and results of laboratory autoclave digestions with NaOH and of mill digestions with sulfate liquors.

Because of the difficulties originally encountered in pulping the entire bamboo culm, the nodes were considered to be more highly lignified than the internodes, as in Savannah grasses, but Raitt found very little difference. His figures for the two follow:

	LIGNIN IN	
	INTERNODES	NODES
Bamboo	15.29	17.60
Savannah grasses	6.13	15.11

The main difficulty in pulping the nodes was found to be the denseness of the material, which retarded liquor penetration. The entire culm is therefore crushed to open up the nodes fully to the action of the liquor and to split the internodes along the capillary tubes, thus eliminating much of the entrained air. This not only renders the nodes usable, but also reduces the buoyancy of the raw material during cooking, eliminates excessive frothing, produces a more uniform digestion of the entire mass, and reduces the digestion time.

TABLE 13

Normal Air-Dry Material		Bambusa arundinacea	Dendrocalamus strictus	Melocanna bambusoides	Ochlandra brandisii
Analysis	Group I. Starches	5.47	5.10	3.15	5.47
	Group II. Pectins	20.13	16.44	17.41	20.53
	Group III. Lignins	15.23	15.28	15.54	14.90
	Group IV. Cellulose	49.17	53.18	53.90	49.10
	Normal air-dry cellulose	54.63	59.09	59.89	54.55
	Ash	2.56	.....	3.05	3.00
	Fat and wax	1.05	.....	....	....
Autoclave	Groups I and II — Temperature, °C., and time, hours	115/2	115/2	115/2	108/2
	NaOH neutralized	10.20	9.50	8.30	10.50
	Groups III and IV — Temperature, °C., and time, hours	158/1 / 140/2	153/1 / 140/2	153/1 / 140/2	153/1 / 140/2
	NaOH neutralized	6.80	6.55	7.70	4.65
	Unbleached pulp	42.1	43.6	45.1	46.4
	Bleached pulp	38.7	40.0	42.2	43.0
	Bleaching powder consumed on raw material	4.20	4.00	3.90	3.57
	NaOH neutralized by Groups I, II, III	17.00	16.05	16.00	15.15
Mill Digestions	Groups I and II — Temperature, °C., and time, hours	115/2	115/2	115/2	108/2
	Liquor density	1.5	1.5	1.5	1.5
	Group III — Temperature, °C., and time, hours	158/1 / 140/2	153/1 / 140/2	153/1 / 140/2	153/½ / 140/2½
	Liquor density	5	5	5	5
	Digestion demand in terms of NaOH	18.0	17.0	17.0	16.0
	Unbleached pulp	42.00	44.41	45.6	47.92
	Bleached pulp	37.80	40.88	42.90	43.30
	Bleaching powder consumed on raw material	3.99	3.67	3.60	3.24

The crushed bamboo culms are cooked by an alkaline process, preferably the sulfate, using a liquor containing 2 parts of NaOH to 1 of Na_2S. Raitt recommends a fractional digestion, which consists of a preliminary weak alkaline treatment to remove starches, gums, sugars, tannins, coloring matters, resins, fats, and waxes, followed by digestion

with a stronger liquor at higher temperature to remove the lignin. The details of the cooking procedure are given in Table 13. Of the four bamboo species in this table, *arundinacea* may be taken as representative of the few inferior varieties, *strictus* and *Melocanna* represent the great majority, and *Ochlandra* is an example of the best.

Raitt also experimented with the digestion of bamboo by the sulfite process; regular calcium bisulfite gave pulp of inferior quality, lower color, and with higher bleach consumption than pulps produced by the alkaline processes, but magnesium bisulfite worked fairly well.

Waste Paper Stock. As a source of fibers, old papers appear to offer many inducements, and it is the opinion of many that they impart to the paper certain desirable, but more or less intangible, properties which are not obtained from new fibers. On the other hand they present problems which must be given careful consideration before their value can be definitely fixed. Among these are the usual ones of cost, uniformity of supply with regard to sorting into different grades, cleanliness, etc., and the more technical ones of ink removal, losses of fillers and fine fibers, color obtainable, and cleanliness and strength of product. Their use in high-grade papers, therefore, necessitates much care and attention.

Grades containing no printed matter offer no special difficulties; unless the papers are very hard sized no alkaline cooking is necessary and they may be pulped in some form of kneader or directly in the beating engine. A common device for this purpose is the Shartle breaker beater, which differs from the usual beater in having the backfall about 8 inches from the roll and also in having no bed plate. The backfall is perforated to permit the passage of good stock but retain trash and rubbish; the good material is then passed to a settling system and thickeners before use. This device is also used in treating printed papers, but not so extensively as for unprinted stock.[19]

The methods employed for disintegrating and cleaning printed waste papers are extremely numerous and vary both mechanically and chemically. Sometimes disintegration and chemical action are carried out in the same equipment simultaneously and sometimes they are separate operations; the treatment given depends somewhat on the grade of paper being handled. A good review of the patents on deinking from 1861 to 1928 is given by Rossman.[30]

According to Shubert[37] one of the first methods of cooking old printed papers was in a stationary cooker fitted with a vomiting pipe for circulation of liquor; this gave poor results owing to uneven penetration of the liquor. Another early method was to cook, defiber, wash, and bleach in a covered Hallander, but the output was small and circulation

not too certain. These methods were followed by rotary boilers for the cooking operation and then by the Winestock process, modifications of which are in general use. The method generally employed is to circulate the stock through the cooking tank by means of an outside centrifugal pump, the discharge from which strikes a target in the tank, thus cooking and defibering in one operation.

Shubert compared rotary cookers, using $3\frac{3}{4}$ per cent caustic on the weight of papers and steaming for 4 hours at 30 pounds pressure, with the circulating cooker, in which the stock is circulated for 2 hours after being treated in a breaking engine for 1 hour with 6 per cent of soda ash, and concluded that the rotary produced a superior product. Milham[25] also studied the deinking process, especially from the standpoint of steam consumption. He calculates that the total steam required per pound of waste paper is 1.37 pounds for rotary cookers and 3.56 pounds for the circulating system. The steam economy, therefore, depends on whether waste heat is available for heating the water in the circulating system. Unlike Shubert, Milham concludes that circulating cookers are preferable to rotaries.

Whatever the method or the grade of papers employed the raw material should be sorted and dusted to remove foreign material and obviously off-grade stock. Staples of magazines may be removed before cooking, or by some sort of pin-catcher or riffler afterward. Sorting is becoming increasingly difficult and important because of the greater variety of special papers and uncookable printing inks and lacquers which are likely to be encountered.

The detergent agents which have been proposed or used for removing the ink include alkalies and alkaline salts, borates, silicates, phosphates, soaps, peroxides, hypochlorites, aluminum chloride, enzymes, and inert materials such as clay, talc, and fuller's earth. These last seem to be added to serve as points about which the ink pigments may gather and thus be more easily washed out. Most inventors are not content with adding single reagents, or even simple combinations of two or three, but often combine as many as eight different substances. It is entirely possible that some combinations may have points of superiority, but for papers with no groundwood the opinion seems to prevail that treatment with caustic soda, soda ash, or sodium silicate in conjunction with soap as a detergent will give as good results as any of the more complicated processes.[9] Some of the newer synthetic wetting and detergent materials also have excellent deinking properties, but most of them are too expensive to use in the cheaper grades of waste papers.

The method of defibering the printed stock has an appreciable effect on the action of the detergent and the efficiency of the subsequent

washing operation. If disintegration of the papers with the detergent takes place in the presence of little water, as in kneaders, the ink pigments seem to be ground into the pores of the fiber and it is almost impossible to wash them out well enough to produce a good color. Disintegration and then dilution before adding the detergent gives much better ink removal, as the pigments tend to rise to the surface and are more readily removed by the washers.

Groundwood papers present a special problem in fiber recovery because lignified fibers are seriously discolored by the alkalies commonly used to loosen the ink. Any detergent agent to give a satisfactory product must avoid this trouble, and experience has shown that none is available at reasonable cost. Wells[40] has attacked the problem from a different angle by depending on a supply of old papers printed with an ink containing the iron lake of hematein as the pigment. These papers are treated in a rod mill to " nodulize " and bring them to a moisture content of 75 to 80 per cent. The stock is then blown to diffusers and treated with sulfur dioxide gas from sulfur burners, after which it is thoroughly washed to remove all acid and is then ready for the paper-making operations.

Washing operations for removal of the loosened ink are carried out in any of the usual devices, ranging from the old drum washers to rotary filters. Methods which turn the stock over and over and expose new surfaces are more efficient than devices forming mats which act as filters to hold back the pigments, but they also cause greater losses of fillers and short fibers. A somewhat novel method of washing is that described by Lewis,[24] in which the disintegrated papers are discharged onto an endless wire belt, inclined slightly upward, above which is another belt supported so as to approach the other gradually and exert pressure. The stock is delivered from the belt into a tank where it is agitated with water and the process repeated until the stock is clean.

The tendency of the pigments to collect as a froth is taken advantage of by Grenaudier,[17] who boils the shredded papers in a 0.1 per cent soap solution and removes the froth as it forms until the stock is practically white. Hines[18] uses a somewhat similar principle by diluting the defibered stock and detergent agents to about 1.25 per cent concentration and treating with a frothing agent in a frothing machine.

The bleaching of the washed stock from old papers involves no new principles and is carried out in any of the common ways. The bleach consumption is low — 3 to 4 per cent of the papers used — and the color attained depends largely on the efficiency of the detergent and washing

operations. Incomplete removal of the ink pigments usually results in a grayish tone.

All the recovery processes involve losses due to the action of the soda and steam in the cooking operations and to the escape of fine fibers and mineral fillers during washing. The combined losses from these causes frequently amount to 35 to 40 per cent of the absolutely dry papers used. Morrison[26] presents figures for average deinking losses as follows:

	PER CENT
Moisture	5.0
Throw-outs	2.0
Dusting	0.5
Screening and riffling	2.5
Deinking	13.0
Bleach washing	2.0
	25.0

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CHAPTER IV

THE SULFATE PROCESS

Paul Hodges

Because of its tremendous growth in the last few years the sulfate pulping process now occupies a position of major importance in the pulp and paper industry. In 1938 the amount of pulp made by this process in the United States exceeded that made by the sulfite and soda processes combined. This growth may be attributed in part to the many new uses for which the strong fiber has proved especially valuable, among the most important being the rapidly increasing use of corrugated and solid fiber shipping containers, as well as bag and wrapping papers. Bleached sulfate fiber is also being substituted for the best grades of sulfite and by its unique properties has made possible many new grades of paper.

The sulfate process is an alkaline process and is so called because alkali lost during the cycle of operations is replaced by sodium sulfate. Actually it is a misnomer, and it would be better to call it the sulfide process because of the important part played by sodium sulfide in the cooking liquor. This sulfide is derived from the sulfate by reduction during the recovery of alkali, and its presence makes the operation of digesters, smelters, and causticizing plants different from that usual in the older soda process.

There is more or less confusion in the use of the terms " sulfate " and " kraft " as applied to the process and products. Sulfate may be considered a general term applying to any cooking process in which the loss of alkali is made up by adding sodium sulfate, while kraft is that subdivision of the sulfate process in which the pulp is intentionally undercooked in order to produce very strong fiber. The products of the sulfate process vary according to the cooking conditions from dark brown, unbleachable kraft fiber, to a soft, easy bleaching stock. Either bleached or unbleached papers made from sulfate pulps range from a coarse, tough, rattly sheet to a soft, pliable, opaque paper depending on cooking treatment and wood. Richter[50] compares sulfate fibers with those of other processes in regard to treatment necessary to apply to paper making.

It has long been recognized that the properties of sulfate pulps were fundamentally different from those made from the same woods by other

processes, Bixler[7] illustrates this difference by the digestion of thin cross sections of wood. Soda and sulfate liquors have selective actions on the ligneous portions of the wood. They remove the intercellular lignin very rapidly but do not visibly attack the cell-wall lignin to any great extent until the former is almost completely removed. Sulfite liquor does not have this selective action, but removes both the intercellular and cell-wall lignin at about the same rate, though much more slowly than the rate at which soda and kraft liquors remove lignin. This may give some clue to the very different behavior of sulfate from other pulps. The reducing action of the sodium sulfide may account for the lower oxycellulose content of the sulfate pulps.

Woods Used. The sulfate process has been applied chiefly to resinous wood such as pine and fir, but because of improvements in sulfate bleaching technique many other woods are now being used. The southern and southeastern pine regions of the United States furnish important supplies of longleaf, loblolly, slash, and other pines. The northwest furnishes hemlock and fir; and in other sections tamarack, jack pine, and spruce are available. Recent additions to the list are gum, sweet gum, oak, maple, and mixed hardwoods, pulps from all of which are being converted into all classes of products from corrugating material through Fourdrinier liners, bag, wrapping, butcher's, semibleached and full-bleached pulp, and, less commonly, highly purified grades of cellulose.

It is generally accepted that straight kraft pulp can be made from almost any kind of wood. Sawmill wastes, turpentine butts (known as " cat faces "), veneer cores, and even extracted chips have been used, but these are of doubtful economy owing to decreased yields and increased chemical consumption. Selective grading of wood is being increasingly discussed but has not yet received the attention in actual practice which it deserves. Most sulfate mills have specifications covering knotty growths, limbs, crooked sticks, small wood, and turpentined faces, but practically no use has been made of the knowledge of the effects of compression wood, growth rate, part of tree, soil conditions, and other factors which affect yield and pulp qualities. Commercial segregation of wood by subspecies and growth rate will come as soon as economical means can be devised, and segregation of wood by density may be even nearer at hand. Serious proposals that wood be purchased on the basis of its cellulose content have appeared in the literature from time to time.

Wood Preparation. Storage of wood has a definite effect on the properties of the pulp it will yield. In the North excellent pulp has been made from wood several years old, but in the South wood deteri-

orates rapidly because of the ravages of insects, decay, and blue stain and other fungus growth. Even in the winter, storage beyond 60 or 90 days is to be avoided, while in wet, hot summer months definite damage to strength and yield can take place within three weeks from the stump. Though the appearance of the wood and "falling of the bark" are usually criteria of deterioration, the only sure means of determining to what extent the wood has been harmed in storage is to make comparative pulpings on a laboratory or commercial scale. The 1 per cent caustic solubility test is also said to have been used with some success.

For the cheaper grades, such as corrugating material, the bark is often left on the wood with no effort to clean it, but Kress and Textor[35] have shown that in a mixture of 96 pounds of wood and 4 pounds of bark the bark used up the equivalent of about 23 pounds of NaOH and 8.5 pounds of Na_2S per ton of bone-dry wood cooked. Another authority states that over a range of 0 to 25 per cent bark the active alkali required per ton of pulp is a straight-line function of the percentage of bark in the charge, increasing at the rate of 13.4 pounds of active alkali for each per cent of bark. For the finer grades of pulp the wood is carefully inspected, knots drilled out, bits of bark removed, scars routed, and logs thoroughly washed before they enter the chippers. Because of the more aggressive action of the chemicals on the dirt and knots it is not necessary to clean the wood as thoroughly as in acid pulping. The worst sources of dirt in sulfate pulp appear to be bark and carbon; the latter is often quite serious in sections where fire protection is poor.

In preparing the wood for use the logs are chipped by running them diagonally against the face of a rapidly revolving disk from which a number of knives project. These are usually from two to four in number, evenly spaced around the disk, but recently chippers have been designed with eight and twelve knives. These are said to have a marked advantage over the others in that the knives are practically in continuous contact with the log, so that it has less chance to jump and the chips are more uniform and contain no slivers. The use of long logs instead of the usual 4-foot length will also reduce slivers, for most of these come when the ends of the sticks are being cut.

The distance to which the knives project from the disk determines the length of the chip, and this is a question which is still much discussed. Since alkaline liquors penetrate the wood much more rapidly than acid, a longer chip may be used than in the sulfite process. This means greater capacity and less power per ton for the chipping equipment, and a greater average fiber length and a higher percentage of long fibers in the pulp. This has been proved by fiber classification

studies, and it is also known that very short chips give inferior pulps. Cable, McKee, and Simmons[14] have shown that between the limits of $\frac{1}{4}$ inch and $1\frac{1}{4}$ inches the length of chip has practically no influence on the yield, bleach required, or loss in weight on bleaching, when cooking aspen, birch, and maple by the soda process.

It is generally conceded that uniform chips mean higher yields and more uniform pulp, and it is therefore important that the chipper room be under strict control. It is also highly probable that chip size and uniformity are closely related to the complete discharge of the stock when the digester is " blown," which is essential for maximum yield and uniformity of product. On the other hand it must not be over-looked that a mixture of over- and undercooked stock, resulting from non-uniform chips, might impart desirable properties in special cases.

After the chipping process the chips go to some form of screen which separates them into three grades — dirt and very fine material, good chips, and slivers and coarse pieces. The dirt and fine stuff is a waste, so far as pulp making is concerned, though it is often used as a fuel in the boiler house. The slivers and coarse pieces are either crushed or rechipped and returned to the screens.

Digesters. The digesters used in the sulfate process are unlined steel vessels, usually welded, and in more recent installations stress relieved and x-ray inspected. The older and smaller digesters were of the tumbling or rotary type, and a number of these are still in use on this continent and abroad, but the upper practical limit for such digesters appears to be about 1500 cu. ft., and the tendency is toward stationary digesters of increasingly larger size. In 1930 a 2500-cu.-ft. digester was considered large, but several modern plants are now using those of 3800- to 4300-cu.-ft. capacity. This upper limit seems to be due to the inability of the railroads to transport larger vessels, but there appears to be no good reason why larger units cannot be fabricated on the plant sites, as is done in sulfite mills.

Rotary digesters are expensive to maintain, inconvenient to relieve and blow, and produce inferior pulp due to the breaking up of the chips in the presence of strong alkali. Stationary, directly heated digesters are low in first cost but wasteful of steam; they produce weak black liquor and, unless a circulating system is provided, are likely to produce non-uniform pulp. Modern indirectly heated, circulated digesters are superior to the others in steam economy, condensate recovery, and ease of operation.

A common type of directly heated digester with a pump for circulating the liquor from the bottom to the top is shown in Fig. 14; Fig. 15 shows one type of indirectly heated digester.

Steam Inlet

Steam Inlet

Liquor
Recirculating
Pipe

Perforated
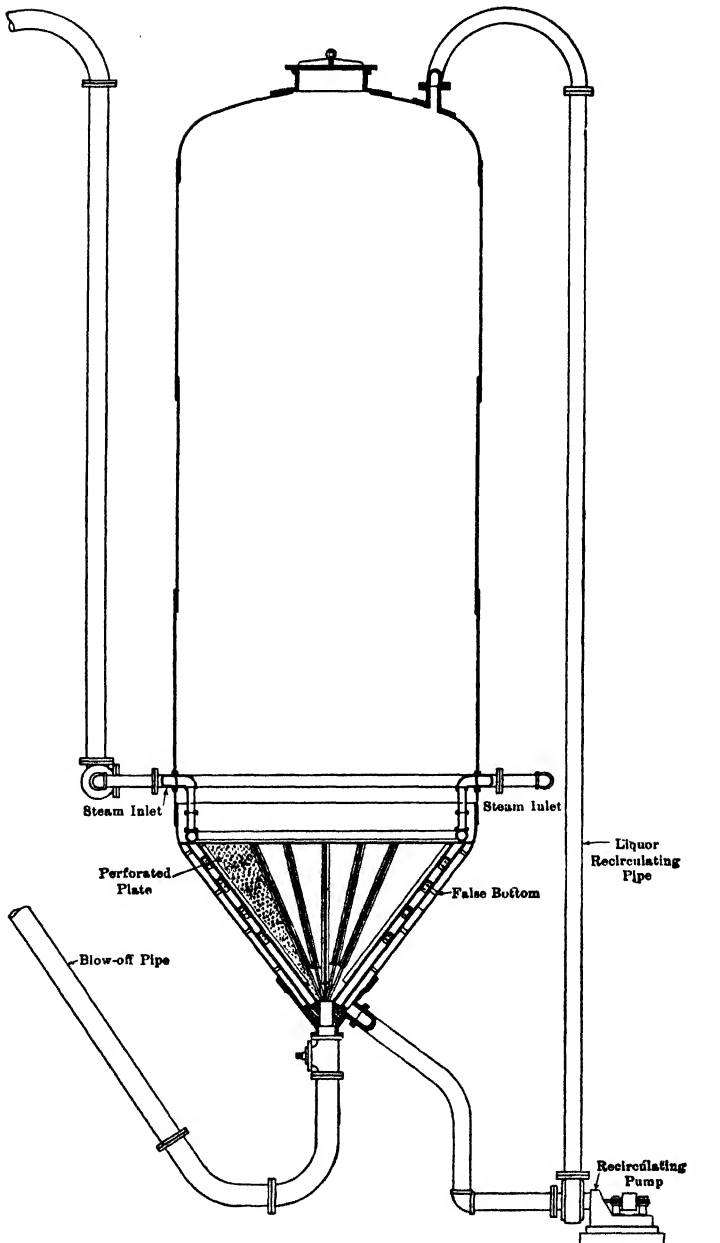Plate

False Bottom

Blow-off Pipe

Recirculating
Pump

FIG. 14. VERTICAL DIGESTER, SECTION SHOWING INLETS, PUMP, AND PIPING.

The results with indirectly heated digesters depend on proper design. Ample circulating capacity is imperative for good operation, and insufficient heating surface or poor trapping of the heaters may cause poor results. Stainless-steel heater tubes are desirable, but ordinary steel or Swedish iron is often used because of lower cost. The only difficulty with stainless tubes is their tendency to scale. Means of shaking up the charge with direct steam should be provided in indirectly heated digesters.

There are various circulating systems for such digesters. The " Morterud " system withdraws the liquor from the bottom and forces it up through the heater and into the digester near the top. The
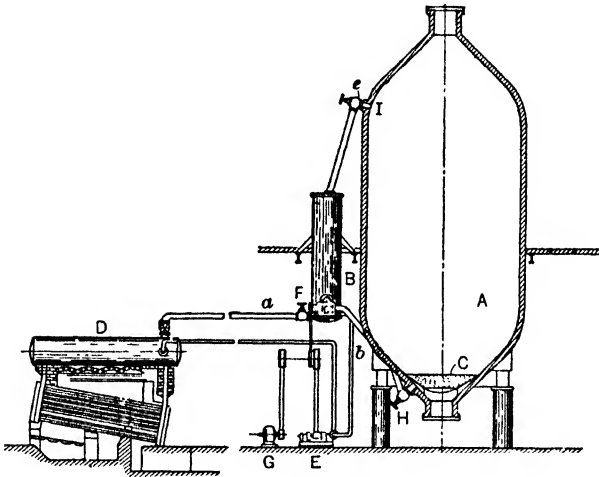

FIG. 15. MORTERUD DIGESTER.

strainer in the bottom of the digester may consist of a false bottom perforated with $\frac{1}{4}$- to $\frac{1}{2}$-inch holes, with a few inches clearance in the cone, or a special fitting in the blow line below the cone, known as a Waern screen. Both methods are quite satisfactory although the latter has the reputation of cleaner blowing of the cooks. In either case direct steam must be connected behind the screen to blow it out when clogged with pulp. It is general practice to blow out for a few seconds three or four times during the cook. The usual heater for the Morterud system consists of a nest of double-tube heating elements. The outer tubes are set with their lower ends in a heavy tube sheet, while their upper ends are closed and free, permitting expansion. The steam enters from below a second tube sheet through the inner tube which discharges near the top of the outer tube. Condensation takes

place on the inside of the outer tube, and the liquor in passing through the heater comes in contact with the outside of the tubes. As this type of heater has inherently low heat-transfer coefficients it is desirable to have excess circulation capacity in the pump in order to increase velocity over the heating surface.

Despite claims to the contrary, it is possible to cook thoroughly and rapidly with this system without the use of direct steam for any purpose other than to blow out the strainers and shake up the charge. Pump motors should be equipped with ammeters to indicate the amount of circulation.

The Schauffelberger system,[52] which is supposed to overcome channeling, takes the liquor out through a perforated belt around the middle and after heating returns it through both top and bottom. The heater is usually a tubular heat exchanger with the liquor flow inside the tubes. These heaters may be single or multipass. High velocities are maintained, and heat transfer is high. The major trouble is to secure uniform circulation to both top and bottom; this can be controlled by flow meters in each line or by empirical setting of the circulation valves.

The " Albenielsen " system,[40] which is a modification of the Morterud system, accomplishes a preliminary concentration by flashing off steam from the heater. The concentrator, which is the basis of the system, consists of a cylinder at the top of which is a conical foam separator surrounded by the steam inlet chamber. At the bottom is another chamber from which the condensate discharges through a two-way valve. There are two condensates, one from evaporated steam, which can be used for washing pulp, and one from fresh steam which can be returned to the boilers. The outlet for the liquor is at the middle of the concentrator.

The digester is filled, the circulation pump started, and liquor passes from the bottom of the digester through the concentrator to the top of the digester. The liquor rises only to the upper edge of the outlet in the concentrator because of air in the upper part. When evaporation is to take place a valve is opened and steam enters the foam separator where the foam bubbles that accompany it burst and fall back into the concentrator, while the evaporated steam goes on to the next concentrator for heating. One concentrator can take care of one or two digesters. The claim for this process is less steam used and the production of black liquor of nearly twice the usual strength. The fiber produced is said to be considerably stronger in tear, stretch, and fold and a little stronger in burst.

Cooking. The cooking cycle in any type of digester consists of three stages: a penetration and pressure-raising period, a full-pressure period, and a gassing-down period; the details of the cooking process are dependent on the type of pulp to be produced and frequently on the personal tastes of the operator.

In the first period a number of processes take place. The air is removed from the digester; the liquor penetrates the chips; the more soluble constituents begin to dissolve and the volatile oils — such as turpentine — begin to distil off with the steam. At a pressure somewhere between 40 and 60 pounds per square inch, reactions involving sulfur compounds take place and the mercaptans and sulfides begin to form. Apparently at this point sulfur combines with lignin to render it more soluble in the alkali, and the rate of delignification increases rapidly. Prior to this the alkali has apparently attacked the more soluble carbohydrate portion of the wood to a greater extent than the lignin. The evolution of non-condensible gases begins to taper off, and the removal of lignin takes place in earnest. As the temperature rises the attack on the cellulose becomes appreciable, but if proper concentration was initially present this attack is inhibited to a large extent by the reduced concentration of NaOH, by the buffer action of sodium-lignin complex, and by the reducing action of sodium sulfide.

It is important that all non-condensible gases be removed from the digester as fast as formed, since false pressures will inhibit steam distillation, and the reaction products remaining in the digester apparently slow down the delignification reaction, but not the degradation of the cellulose. It is common knowledge among digester operators that if a digester is not sufficiently relieved the pulping reaction may be so slowed up that undercooked and inferior pulp may result.

In practice it is sometimes necessary to " bank " or "shut in " a cook because of lack of blow-pit capacity. This is done by closing the relief valve, shutting off the steam, and stopping circulation; for the best results it should be done before 80 pounds pressure is reached. If the pressure rises more than 5 pounds above the steam table pressure for the corresponding temperature, the digester is relieved slightly. In well-insulated digesters closing the relief at a point of high reaction rate will cause a sudden rise in temperature and pressure due to the heat of reaction, and if this is not taken care of by relief dangerous pressures may result. It is equally important to see that the pressure does not fall, owing to radiation; if necessary a small amount of direct steam is used to maintain it at the right point.

The period at low temperature is sometimes prolonged to allow the chemicals to penetrate the wood. This is common practice in Scan-

dinavian mills cooking for strong kraft fiber, where such impregnation periods varied in 1930 from 20 minutes to an hour at gage pressures of 28 to 70 pounds. It is said that such practice gives more uniform and stronger pulp. Wells[62] claims that by an impregnation of, the chips with cooking liquor under pressure, and then removal of much of the liquor, the chemicals required may be reduced as much as 16 per cent, the yield increased about 4.5 per cent, and the steam consumption for cooking and evaporation materially reduced. Woodhead[64] states that impregnation of the chips with black liquor decreased the consumption of chemicals, saved evaporation, increased the yield, and gave greater strength to the kraft paper made.

When full pressure is reached — usually 100 pounds but sometimes as high as 135 pounds — generation of gases in the digesters is relatively small. Delignification proceeds at a decreasing rate as alkali is consumed and the less readily soluble lignin is to be removed. It is possible to produce good pulp with no " full cooking pressure " period. In this case the temperature is raised slowly over the entire time, and the cook is " blown " when maximum pressure is reached.

The gassing-down period consists of the reduction of pressure by top relief until some specified pressure is reached (usually around 60 pounds gage) and then " blowing " by opening a valve in the bottom of the digester. This is usually done to allow more time to absorb heat from the " flashed " vapors, to recover last traces of turpentine, and to prevent damage to fibers by excessive " explosion." In many mills this gassing-down period is omitted, the cooks being blown at full pressure in 8 to 20 minutes. Apparently it is felt that the gains mentioned above do not compensate for the loss of digester time entailed.

Steam Consumption. The steam consumed in alkaline cooking processes depends on the capacity of the digester, the efficiency of its insulating covering, the concentration of the cooking liquor and its amount, the temperature of the cook, and whether steam is applied directly or indirectly. During the penetration and pressure-raising period the demand for steam is very great, but after pressure is reached only enough is required to make up for the heat lost by radiation.

A detailed evaluation of the heat input for alkaline pulping digesters in eleven Canadian and United States mills has been made by Murdock,[47] who found the average steam consumption per ton of pulp to be 4135 pounds when the steam supplied was at 125 pounds pressure and not superheated. Moon[45] states that approximately 3,300,000 B.t.u. per ton is required to bring the digester and its contents up to temperature, and that of this amount 2,700,000 B.t.u. is liberated

in the blow-off steam and can be recovered and used in furnishing hot water.

Records obtained by steam flow meters on two old-type rotary digesters and a modern vertical, stationary digester using direct steam gave the following results in pounds of steam required:

	Steam Required in Pounds per Hour		
	3-Cord Rotary	6½-Cord Rotary	15-Cord Stationary Digester
Pressure-raising period..	7500–7800	10,800	20,000–22,100
Period at pressure...	500	1,050	1250*
Total during cooking period.......	12,125	19,360	37,750–44,250

* Calculated by radiation formula for steam pipes.

Much attention has been given to the recovery of heat from digester gassing and blowing, and various exchange heaters have been designed for the purpose. The distribution of heat in blowing has been investigated by Tomlinson and Collinge,[59] who state that approximately 85 per cent of the heat can be usefully absorbed in pulp-mill operations, and the 15 per cent loss is distributed as:

	Per Cent
Uncondensed steam	1
In water to sewer	3
Radiation from liquor system	10
Radiation from blow tanks	1

Pulping Variables. The variables of the sulfate cooking process have received much discussion, but there is relatively little reliable published information. Among the factors which are known to affect the quality or yield of the resulting pulps are species of wood, characteristics of chips, ratio of chemical to wood, concentration of chemical, composition of cooking liquor, time to raise pressure, time at pressure, maximum temperature, and relief schedule. Many other possible variables might be mentioned, but when carrying out experiments involving several, it is difficult to obtain reliable data on any particular one.

Schwartz and Bray,[50] in summarizing work done at the Forest Products Laboratory, state that the rate of pulping is increased by increasing the temperature of digestion, the ratio of chemical to wood, and the initial concentration of chemical in the cooking liquor. It has been shown that liquors of comparatively low concentration suffice for pulp-

ing and that increasing the ratio of chemical to wood beyond 30 per cent is not justified by increase in rate of digestion and pulp purity. From the standpoint of fiber properties the best procedure would be to cook at the lowest possible temperature and chemical concentration — and hence the longest digestion time — with an infinite chemical-to-wood ratio; but from the standpoint of economy cooking should proceed at the highest possible temperature and chemical concentration — and hence the shortest period of digestion — with the lowest possible chemical-to-wood ratio. It is obvious that the same quality of pulp may be produced by several different combinations of these conditions.

Actual cooking data for a number of plants operating on different kinds of wood and producing different grades of pulp are given by Murdock.[47] More recent data over a wide range of products, all with modern circulating systems, are given in Table 14.

TABLE 14

	Volume per Ton Exclusive of Moisture in Wood	Active Alkali	Time to Pressure	At Pressure	Sulfidity
	Gal.	Lb.	Hr.	Hr.	Per cent
1. Kraft liner board, pine....	1000	650	1:15	1:45	30
2. Kraft bag, pine..........	1100	630	1:25	1:35	30
3. Bleached Western hemlock.	1730	690	1:30	1:45	35
4. Bleached pine............	1450	740	3:15	2:00	28
5. Bleached red gum........	1400	670	2:25	1:50	20
6. Kraft, Swedish, pine	1260	480	4:00	3:40	29

Note: In this chapter the standard terms of the sulfate process as defined in Official Standard O 400p of the Technical Association of the Pulp and Paper Industry are used. The total chemical in a cook is all sodium salts expressed as Na_2O. The total alkali is $NaOH + Na_2S + Na_2CO_3 + Na_2SO_4$, all expressed as Na_2O while the active alkali is the $NaOH + Na_2S$ given as Na_2O. The sulfidity is found by dividing the sulfide expressed as Na_2O by the total titratable alkali ($NaOH + Na_2CO_3 + Na_2S$ expressed as Na_2O).

The white liquor is generally prepared at a concentration of about 120 grams per liter of total Na_2O, and as this is stronger than is needed for the digester charge it is diluted to the proper volume with black liquor of 1° to 4° Bé. at 40° F. This is done to conserve the alkali in the black liquor which is too weak to be economically concentrated by evaporation, to keep this liquor from being dumped into streams, to utilize heat, and possibly to accelerate penetration slightly

in fast cooks. Claims have been made as to the catalytic effect of this liquor, but actual experiments which definitely prove such a phenomenon are lacking. It can be shown that for easy bleaching pulps better brightness with less loss of strength can be attained by diluting the white liquor with water, and this is made feasible with the complete recovery of black liquor in the modern washing systems.

The longer the pressure-raising period the less the action of the alkali on the cellulose and hence the less degraded the resulting pulp. Thus a slowly steamed pulp should have a high initial tear and should develop a good burst on beating. This is probably due to the fact that the major part of delignification takes place at low temperatures, and that the concentration of hydroxide is less when full pressure is reached. This modifies the action of the alkali and degradation of cellulose is greatly reduced.

In a rapidly steamed cook considerable alkali is present when top temperature is reached and cellulose is degraded to a greater extent. In kraft bag and board stocks, where a high degree of delignification is not desired, less alkali is used and the temperature is brought up rapidly. This likewise results in a low concentration of hydroxide at full pressure and in a stong pulp. Prolonged cooking of this pulp will not cause as complete removal of lignin as with cooks using more alkali.

Studies of the maximum cooking temperature by Hägglund and Eidem[24] showed no advantage in lowering it below 338° F., either in yield or quality of pulp. Temperatures below 320° F. required excess alkali to produce properly cooked pulp, while above 345° F. little was gained except to speed up the reaction. Work by Martin, Bray, and Curran[41] on two kinds of pine, under varying conditions of time and temperature (320°, 348°, 360°, and 366° F.), showed that there was no particular critical temperature which was noticeably beneficial or otherwise; the pulps cooked to the same yields were found to be very similar. According to Bray[9] a rise of 10° C. (18° F.) doubles the speed of reaction.

The ratio of chemical to wood has been investigated by numerous workers. Curran and Bray[16] concluded that a high ratio and a low concentration of chemicals produced a pulp which was best for bleaching. Bray, Martin, and Schwartz[11] varied the ratio of chemical to wood between 15 and 25 per cent and concluded that increasing the ratio increased the percentage of chemicals consumed, made a marked decrease in total yield and screenings, and increased the degree of delignification, at the same time causing large changes in bleachability of the resulting pulps. The maximum yield was obtained between 18.75 and 20 per cent, and beyond 20 per cent the destruction of cellu-

lose proceeded faster than removal of lignin. Recent data by Hansen[27] tend to show that the optimum ratio of chemical to wood depends on the sulfidity of the cooking liquor. Stevens[57] says, "Apparently the concentration governs the yield and the alkali ratio determines the quality of pulp for a given cooking cycle."

The effect of concentration of chemical has been investigated by Bray and Curran,[10] who show that increasing the concentration increases the rate of pulping, decreases the yield, and gives pulps with lower alpha-cellulose content and probably lower strength and viscosity. Studies by the Canadian Forest Products Laboratory[1] on soda cooks have shown that high concentration of caustic soda (40 per cent solution) affects the character of the cellulose aggregate, decreasing it in size, and resulting in lower viscosity and alpha-cellulose content.

If a portion of the alkali in a soda cook is replaced by sodium sulfide the pulping action is accelerated, the yield, strength, and color of the pulp are improved, and its lignin content is lower. Kress and McGregor[33] believe that 2 parts of NaOH to 1 of Na_2S will produce an unbleached pulp of good strength and with screenings sufficiently softened so that they can be reduced by mechanical means. Their experiments revealed that a greater total yield is obtained on increasing the sulfidity, but beyond certain fairly well-defined limits the yield of pulp decreases and screenings increase. Johansson[28] found that a 3 to 1 ratio caused the greatest removal of lignin and consequently a pulp of lower bleach requirement. Hägglund and Hedlund[25] found that an increase in the sulfide content up to 16 per cent hastened the pulping action and reduced the lignin content. Bray, Martin, and Schwartz[12] show that, by keeping the NaOH content at 20 per cent and varying the hydrosulfide, the yield and bleach requirement of pulps from Douglas fir cooks decrease progressively up to sulfidities of 34 per cent, but that further increases in sulfidity up to 100 per cent result in only slight changes in yield and quality.

Surface and Cooper[58] state that "With each different combination of the cooking conditions there is a minimum amount of sodium sulphide which must be used with the caustic soda present to impart to the product the high strength and good wearing properties characteristic of properly cooked sulphate kraft pulp." Work by Hansen[27] indicates that for each alkali-to-wood ratio there is an optimum sulfidity, and that though a total chemical of 12 per cent may be effective at no sulfidity, it requires 40 per cent total chemical to be effective at 220 per cent sulfidity, or a straight sodium hydrosulfide cook. At 19 per cent total chemical, 40 per cent sulfidity is indicated; and at 25 per cent total chemical, 76 per cent sulfidity is required.

It thus appears that any sulfidity requires a definite quantity of hydroxide present in order to carry out delignification satisfactorily. Mitchell's data[43] tend to substantiate this statement. He observes that the diminution of the pulping power of kraft liquors at high sulfidities is noted only when the conditions of the experiment are close to those in commercial practice. He points out that Kress and McGregor[33] obtained poor delignification at high sulfidities because they worked at a fixed total chemical, and consequently at the higher sulfidities insufficient alkali was present.

Yields. It is difficult to give any very definite figures for pulp yields in the sulfate process because they are so influenced by operating conditions. Good yields for spruce and fir seem to run around 38 to 42 per cent on the bone-dry basis, while southern pine gives about 42 to 50 per cent and gum 48 to 52 per cent, depending on the type of pulp made.

Cooking Liquor. The cooking or " white liquor " used in the sulfate process has as its principal active constituents sodium hydroxide and sulfide, and if sulfur is used as an auxiliary chemical, one or more of the sodium polysulfides is also present. Sodium carbonate, sulfate, silicate, aluminate, sulfite, and thiosulfate occur in smaller quantities as relatively inactive components. Sodium sulfite and thiosulfate occur frequently when weak liquor is used to scrub recovery stack gases and have been suspected of having an adverse effect on pulp strength. With the exception of the work of Aronovsky[3] and Aronovsky and Gortner[4] little has been published on the effects of minor constituents. The ratio of sulfide to hydroxide varies over a wide range. From 20 to 35 per cent of the total alkali in the sulfide form is usual, but in actual practice liquors can be found ranging from pure soda liquor up to 45 per cent sulfidity. Lower sulfidities are usually indicative of low alkali losses and consequently low salt cake consumption, but the use of soda ash as an auxiliary chemical may produce the same result.

The following analyses of undiluted liquors are given for several mills:

	GRAMS PER LITER		
	A	B	C
Na_2CO_3	19	17	19
Na_2S	26	22	41
$NaOH$	71	77	68
Na_2SO_4	1.7	2	1.7
$Na_2S_2O_3$	2.5	2.5	6.2
Na_2SO_3	6.0	0.24	1.1

Relief Gases and Odors. Gordon and Creitz[23] have studied the odor problem in sulfate pulp making and list the possible sources of odors as: (a) relief of digesters during cooking; (b) blowing-down pressure prior to and during discharging; (c) the condensate from the evaporators; and (d) occasionally too low solids in the black liquor being sprayed into the furnace, which may cool it too much and allow mercaptans to escape combustion.

The relief gases from the digesters have been studied extensively in Sweden and Germany. Bergström and Fagerlind[6] have found them to contain methyl mercaptan, dimethyl sulfide, dimethyl disulfide, methyl alcohol, ammonia, turpentine, rosin oil, hydrogen sulfide, ammonium sulfide, and acetone. The unpleasant odors are due in large part to the first two compounds, of which mercaptan is far the worse. According to Klason and Segerfeld[31] about 100 grams of mercaptan are produced per ton of wood treated in making easy bleaching pulp, while ten times as much may be obtained in kraft cooks. Pine yields about twice as much as spruce. According to Falk[18] the condensed materials per ton of cellulose from pine wood are as follows:

	In Oil Portion Kg.	In Aqueous Portion Kg.
Mercaptan	0.062	0.06
Dimethyl sulfide	0.927	0.17
Dimethyl disulfide	0.103	0.05
Turpentine	8.487	0.92
Distillation residue	0.721	....
Methyl alcohol	....	5.00
Ammonia	....	0.18

From work done at the Billingfors mill the condensed steam from the digesters was found to yield the following quantities for every ton of finished pulp made:

	Pounds
Turpentine	17.6 (from fir)
Turpentine	2.2 (from pine)
Methyl alcohol	11.0
Methyl mercaptan	2.2
Methyl sulfide	6.6
Methyl bisulfide	0.2
Ammonia	0.4

Klason[29] has carried out extended investigations of the sulfate process in the attempt to eliminate odors. He found that the gases could be almost entirely freed from mercaptan by passing through solutions of

various metallic salts, but that the only metallic mercaptides which were completely odorless were those of the noble metals. Caustic soda will also absorb mercaptan, but not methyl sulfide. The gases separated from entrained liquid can be rendered harmless by passing them under a furnace grate, but explosions must be guarded against. Oxidizing agents, as bleach or permanganate, will destroy the odors, but they also oxidize the alcohol and the quantity is therefore excessive. Gordon and Creitz found chlorine effective, but about 25 pounds per ton of pulp was necessary. Schwalbe[55] removed odors by passing the gases through wood or straw and subsequently using these to produce pulp.

The most practical way to reduce odors appears to be to scrub the gases in a barometric spray condenser with aerated water, collect all non-condensibles and pass them through the blow pipes in the recovery furnace where they will burn. In mills making bleached fiber the condenser effluent may be mixed with waste bleach plant waters containing traces of bleach, but even without this precaution no serious nuisance is created with proper operation. In modern recovery operation combustion is usually so good that all mercaptans and organic sulfides are destroyed unless a black liquor scrubber is used.

Blowing. At the completion of a cook the contents of a rotary digester consist of material thoroughly reduced to the fibrous condition, while that in a stationary digester still retains very largely the shape of the original chips. Rotary digesters are discharged by blowing off pressure until the heads can be removed and then dumping the contents by revolving the digester. Vertical digesters are emptied by blowing the entire charge through a pipe leading from the bottom of the digester to a blow pit or some form of steam separator. This may be done at full cooking pressure or after reducing this to 80 pounds or less by blowing off steam. This latter method takes more time but permits of better steam recovery and is claimed to give more complete blows because the steam relief tends to loosen up the charge and make it flow like a viscous fluid.

A very satisfactory device for separating steam from stock when blowing a digester is shown in diagram in Fig. 16. The stock enters tangentially at such high speed that it hugs the wall of the separator while the steam escapes to the center and out through the ventilator, or to some form of condenser. On blowing the charge the sudden release of pressure causes violent evolution of steam from the moisture in the chips, and this, together with the mechanical action of passing through the pipe, causes complete disintegration into the fibrous state. The separator is usually placed at an elevation higher than the top of the

digesters and the stock therefore drops by gravity to the washing equipment.   At this point it contains the fiber, all the alkali originally added, the organic matter dissolved during the cook, and a large amount of water, both from the liquor added and from condensed steam if direct steaming is practiced.
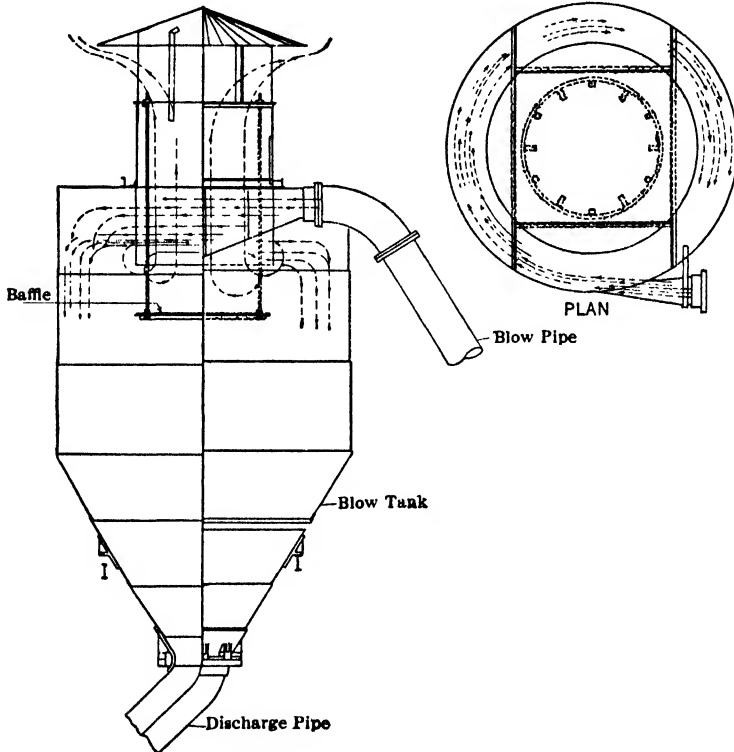

FIG. 16.   BLOW TANK OR SEPARATOR.

Washing.   The separation of the fiber from the black liquor and the washing of the fiber to remove the last traces of liquor are carried out in diffusers or open wash pans.   A diffuser is a large vessel, about the volume of a digester or a little larger, with a perforated false bottom through which the liquor passes.   It is made of steel, and must be constructed to stand the pressure of the water used during washing. The washing is most efficient when a plunger of hot water forces the liquor out of the bottom with a minimum of channeling and dilution.   If properly carried out this type of washing recovers the major portion of the black liquor with little dilution, clean stock may be had without

resorting to series washing, and the weak black liquor is kept at such a volume that it just furnishes that needed for dilution of the next cook. Much depends on the proper design and operation of the diffuser; if it is improperly designed and operated series washing will be necessary with accompanying loss of time and large volumes of weak liquor to handle.

The pressure of washing is an important factor in diffuser operation. A freshly blown sulfate fiber will float, but as pressure is applied it acts like a Cartesian diver and sinks. If still higher pressure is applied the gases escape from the fiber capillary and it becomes permanently dense. All this has its effect on the flow of liquid through the fiber mat. The maximum desirable pressure is from 30 to 40 pounds per square inch, depending on the type of fiber.

Wash pans are in effect open diffusers and their action is quite similar, though they are not so versatile as they are operated only at atmospheric pressure.

Recent practice tends toward the use of rotary filters for washing. Morrison[46] claims that the foaming of black liquor is negligible unless considerable volumes of air are intimately mixed with it, and the foaming troubles of the early installations have been overcome. Multistage, counter-current washing with three units in series gives better results than single filters, and the major factors in successful operation are accurate regulation of feed to give uniformity, and a smooth, even formation of the sheet. Control of liquor temperature and vacuum so that no flashing occurs in barometric legs to cause foaming is also important. Morrison gives the washing loss on filters as less than 60 pounds of salt cake per ton of fiber as compared with about 110 pounds for diffusers, and claims that filters give a liquor to the evaporators which is about 1° Bé. stronger than from diffusers. Under superior operating conditions the total washing loss may be as low as 40 pounds of salt cake per ton of fiber.

Other methods proposed for washing pulp include screw presses, the Kuntztown press, and the centrifugal extractor, but these do not yet appear to be developed to a commercially economical stage.

Screening. After washing the pulp is usually dumped or sluiced into an agitated storage chest where further soda is removed by soaking. The pulp is then passed through knotting screens, or " knotters," which are usually centrifugal screens with holes from $\frac{1}{8}$ to $\frac{1}{2}$ inch in diameter, and then through finer screens. These fine screens for kraft are usually centrifugal with holes 0.125 inch in diameter, while in the bleached grades they consist of flat screens with slots from 0.008 to 0.018 inch. Flat screens are sometimes preceded by rifflers or " sand traps." Sulfate

screening is usually carried out at a consistency of 0.2 to 0.4 per cent.

In many mills screenings and knots are put back into the digesters and cooked, but this practice is of doubtful economic value. In board mills they are frequently put through mills or refiners and used in liner board or in the inner sheets of cylinder board. In the manufacture of bleached pulps the volume of screenings is relatively small, owing to thorough cooking, and they are usually sent to the sewer.

Of major importance in proper screening is the prevention or control of the foam caused by alkaline liquors. Good washing is the obvious answer, but it is frequently necessary to use a foam killer, which is generally kerosene. This should always be used in moderation as it can be definitely shown to affect the sheet-forming properties, probably by coating the fibers and interfering with bonding. A number of other products are sold for this purpose and are more effective than kerosene, but few are as economical. Acidification or the reduction of pH is frequently effective, as are also changes in design which eliminate air.

Another serious trouble in screening is the formation of scale from the use of hard water, particularly where it is diluted with white water containing alum, size, or bleach residues. This is usually dealt with by souring with acid or steaming, though often redesign of the white water system is the only cure.

Black Liquor. The black liquor removed from the fiber during washing contains nearly all the chemicals employed, together with the organic matter from about half the weight of the wood. According to Klason and Segerfeld[31] the organic matter consists of 54.3 per cent lignin, 2.5 per cent fatty and rosin acids, 3.7 per cent formic acid, 5.2 per cent acetic acid, and 30.3 per cent lactonic acids. Of the sulfur originally present as alkali sulfide, 51.8 per cent was combined with lignin, 15 per cent expelled as volatile compounds, 16.8 per cent remained as alkali sulfide, and 16.4 per cent was unaccounted for. Except for the fact that the sulfur combined with the lignin appears to be a function of the sulfidity of the cooking liquor, recent data tend to confirm these findings.

Kress and McIntyre[34] studied the sulfur balance by means of rotary autoclave cooks and found about 14 per cent of the sulfur unaccounted for in the black liquor. Later work, under more accurate conditions, showed that the sulfur charged was distributed as follows:

	PER CENT
In black liquor	48.8
In washings	41.2
In washed pulp	1.8
In condensate of relief	7.4
In absorption towers for mercaptans	0.05
Unaccounted for	0.75

They found little change in the Na_2S content of the black liquor after the first 60 minutes of a 3-hour cook.

The following analyses of sulfate black liquors, expressed in grams per liter, are given by a committee appointed by the Finnish Government[19] and by Cirves:[15]

	FINNISH GOV'T	CIRVES
Sodium carbonate (Na_2CO_3)	27.5	14.78
Sodium hydroxide (NaOH)	4.5	1.43
Sodium sulfide (Na_2S)	17.6	3.01
Sodium sulfate (Na_2SO_4)	12.1	14.70
Sodium sulfite (Na_2SO_3)	1.6	6.64
Sodium chloride (NaCl)	1.7	.88
Sodium thiosulfate ($Na_2S_2O_3$)	1.4	3.98
Sodium silicate	....	1.52
Soda combined with organic acids	22.5	14.52
Organic acids	117.1	92.49
Water, etc.	794.0	846.05

Evaporation and Recovery. The present economic advantage of the sulfate process depends largely on the ease of recovery of cooking chemicals. Efficient operation of the " liquor cycle " consists of washing the black liquor from the pulp with as little dilution as possible, evaporating this to a readily combustible condition with minimum steam, burning with maximum recovery of heat and sodium salts, conversion of a maximum percentage of sodium sulfate to sulfide, highest possible conversion of sodium carbonate to hydroxide, separation of mud with minimum loss of sodium salts, and the delivery of hot, clear " white liquor " to the digesters.

Black liquor was formerly evaporated in disk evaporators, gases from the smelter being used as a source of heat, and then passed through a rotary dryer which converted it to a thick, syrupy fluid, a gummy mass, or a black ash, depending on the installation. It was then mixed with salt cake and shoveled into the smelter where combustion and reduction took place.

In present practice the weak liquor with 12 to 20 per cent solids is passed into multiple-effect evaporators, which operate on the principle that the boiling point of the liquor is lowered by reducing the pressure under which it boils. In these evaporators the steam from the liquor evaporated in the first effect serves to boil the liquor in the second effect, this being kept under low enough pressure so that active ebullition takes place. The steam from the second effect heats the liquor in the third, and so on through the system of three to five or more effects. The only heat from outside sources is therefore in the first effect, in which the liquor is raised from its entering temperature to that of

ebullition at the pressure in this effect. The vacuum is maintained by means of a condenser and pump, and the concentrated liquor is removed from the last effect by another pump, which usually discharges into a tank which supplies the furnace or burner. In sulfate mills it is customary to change the order in which the liquor passes the effects so that the strong liquor is in the first effect, as a higher temperature is necessary to keep its viscosity low.

Both horizontal and vertical tube bodies are used. In recent installations the trend has been almost wholly to film-type, vertical-tube evaporators, usually piped for four or five steam effects. Six-body quintuple and seven-body sextuple effect evaporators are becoming common practice, the extra body being used in parallel with the heavy liquor effect.

The vertical film-type evaporator body usually has tubes $1\frac{1}{4}$ to 2 inches in diameter and 14 to 22 feet long. For this reason they are sometimes called long-tube evaporators. Since this type is the result of an endeavor to eliminate hydrostatic head as far as practicable, and thus reduce the boiling point in each effect, it gives a higher working temperature drop and a higher capacity per unit of heating surface than any other type except forced circulation. Making use of the inherent foaming qualities of black liquor, which give so much trouble in other types, the high vapor velocity tends to carry liquor along in the form of foam and bubbles, producing high-velocity filming action on the heating surface with phenomenally high heat-transfer coefficients. Efficient head design gives complete recovery of foam as liquor, and with good operation and maintenance the liquor loss from these evaporators is practically nil.

In some installations the evaporated black liquor at 50 to 60 per cent solids is passed into single-effect, forced-circulation concentrators where by means of high-pressure steam (usually 150 pounds) it is further concentrated to 70 and even 80 per cent solids before being burned.

The steam economy of evaporators is affected by so many conditions that only a few generalizations can be made. Experience has shown that triple-effect evaporators obtain from 2.0 to 2.4 pounds of evaporation per pound of steam used, while a quadruple-effect will evaporate 2.8 to 3.5 pounds. These efficiencies are considerably affected by the order in which the liquor passes the effects, and the highest efficiency in the evaporator may not be the best when the heat economy of the whole mill is considered.

The control of evaporation is usually done with a hydrometer calibrated in the Baumé scale. This is used because the total solids and Baumé are almost a straight-line relation. While this relation varies

from mill to mill, per cent total solids is usually equal to one and one-half times the Baumé reading at 60° F. Evaporators should be equipped with liquor and steam flow meters and a liberal supply of recording thermometers.

The effect of temperature on the Baumé reading of sulfate black liquor from a northern mill is shown in Table 15.

TABLE 15

Temperature in degrees C.								
10	20	30	40	50	60	70	80	90
Degrees Baumé of Black Liquor								
28.2	27.8	27.2	26.5	26.0	25.2	24.5	23 7	22.9
26.2	25.8	25.2	24.5	24.0	23.2	22.5	21 7	20.9
24.2	23.8	23.2	22.5	22.0	21.2	20.5	19.7	18 9
22.2	21.8	21.2	20 5	20.0	19.3	18.5	17 8	17.0
20.2	19.8	19.2	18.5	18.0	17.2	16.5	15.8	15.0
18.2	17.8	17.2	16.5	16.0	15.3	14.5	13.8	13.0
16.2	15.7	15.1	14.4	13.9	13.3	12.5	11.8	11.0
14.2	13.7	13.2	12.5	12.0	11.3	10.5	9 7	8.9
12.2	11.7	11.2	10.5	9.9	9.3	8.5	7.8	7.0
10.2	9.7	9.2	8.5	7.9	7.3	6.6	5.8	5.0
8.2	7.7	7.2	6.6	6.1	5.3	4.6	3.8	3 0
6.2	5.8	5.4	5.0	4.4	3.7	3.0	2 3	1.7
4.2	3.8	3.4	3.0	2.4	1.9	1.1	0.4	−0.2
2.2	1.8	1.4	1.0	0.6	0.0	−0.6	−1.2	−1.5

After concentration the liquor is pumped to the recovery furnace, of which a number of types are in use. The older type, or black-ash furnace, is illustrated in Fig. 17. It consists of a revolving, cylindrical shell, lined with hard-burned red brick to a thickness of 15 inches at the end where the liquor enters and about 9 inches at the discharge end. This causes the material to work gradually from back to front of the furnace, at which point the burned ash is discharged, ready to be mixed with the necessary salt cake and shoveled into the smelters, from which the molten smelt flows through a spout into a dissolving tank. Black-ash furnaces are generally about 20 feet long and 9 feet in outside diameter, but some are as much as 30 feet long. They are mounted on wheels and caused to turn at a speed of one to three revolutions per minute.

In this type of furnace the strong black liquor from the evaporators, which enters the back of the furnace, is not concentrated enough to support its own combustion, but as it works forward in the furnace it
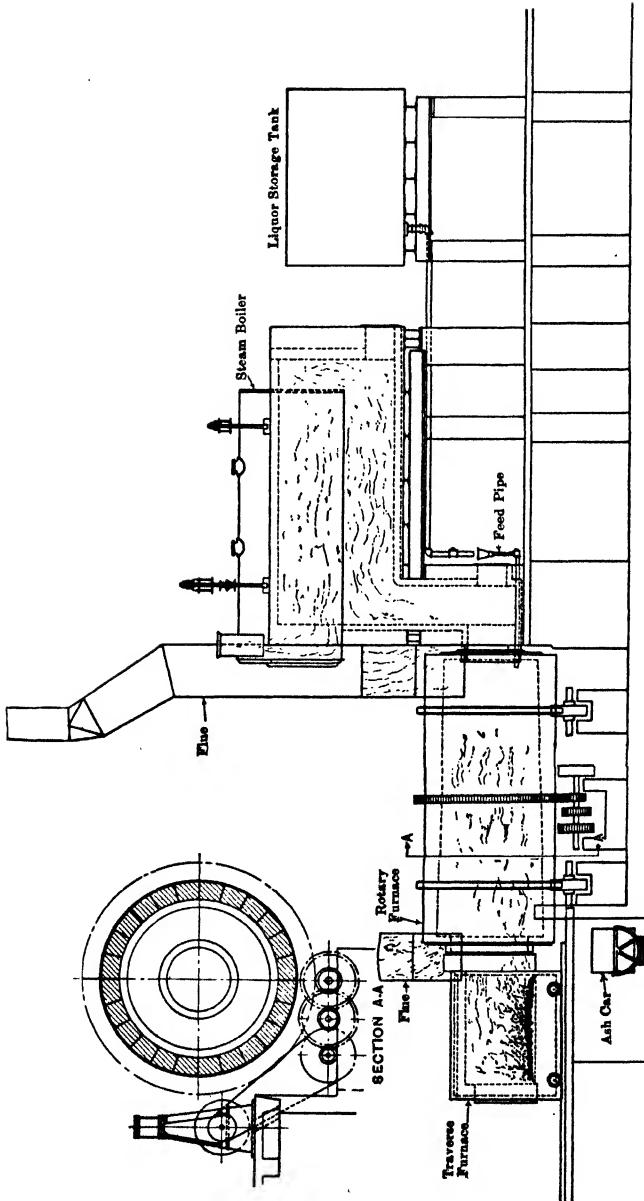
Fig. 17. Soda-Recovery or Black-Ash Furnace.

loses water and finally burns. Some heat usually has to be supplied to these furnaces, and this is done by means of a fire box, or traverse furnace, mounted on wheels so that it can be drawn back when the rotary portion needs repairs.

The Murray-Waern system is a modernization of the rotary type. In this the black liquor, containing the necessary salt cake in solution, passes through an evaporator-scrubber where it is concentrated from about 35 to about 50 per cent solids by means of flue gases from the waste-heat boiler, and during the process reduces the chemicals lost in the latter to about 50 pounds of salt cake per ton of pulp. From the evaporator it passes to a rotary dryer, through which the gases from the smelter pass on their way to the waste-heat boiler, and the solid residue is delivered to the smelter pot, into which air is blown through water-cooled nozzles. Air is also admitted through a forced-draft fan and around the neck of the rotary where it protrudes into the smelter pot; the amounts must be carefully regulated to give proper combustion and reduction of sulfate.

The Ross-Wagner furnace[60] consists of a single vertical furnace chamber within which all the recovery processes are performed. The furnace is approximately 30 feet high and 12 to 14 feet square with a lower smelter section approximately 13 feet in diameter. Black liquor containing 60 to 70 per cent solids is sprayed in through a nozzle in the roof. As it falls through the furnace it is evaporated to ash by the rising hot gases. A fuel bed of black ash is formed in the smelter to a considerable depth, and primary air is introduced through water-cooled nozzles into this fuel bed, where both reducing and smelting operations take place. The pool of smelt formed at the bottom is discharged through a water-cooled spout.

The furnace is supplied with water-cooled walls and top, and the boiler is usually a three-drum Stirling type. Salt cake is fed in as a dry powder or mixed with the liquor before spraying.

The Goodell system dries the black liquor in a spray dryer heated by the exit gases from the furnace. The resulting powdered fuel, containing approximately 2 per cent of moisture, is fed into the furnace where burning, reduction, and smelting take place. The smelt flows out of the smelt notch from a sloping floor into the dissolving pit. The boiler is much the same as the Wagner. The carry-over from the spray dryer is scrubbed by the incoming black liquor in a concentrator-scrubber, which raises the solids in the black liquor from 45 to 55 per cent, at which strength it goes to the spray dryer.

The Tomlinson furnace,[63] shown in Fig. 18, consists of a rectangular furnace with walls of water tubes, lightly coated with a plastic refrac-

tory, and follows in general the design of recent pulverized-fuel steam boilers. The liquor is sprayed into the furnace through nozzles designed to deliver uniform drops of considerable size. The nozzles have an oscillating motion, and the drops strike the back and side walls to a
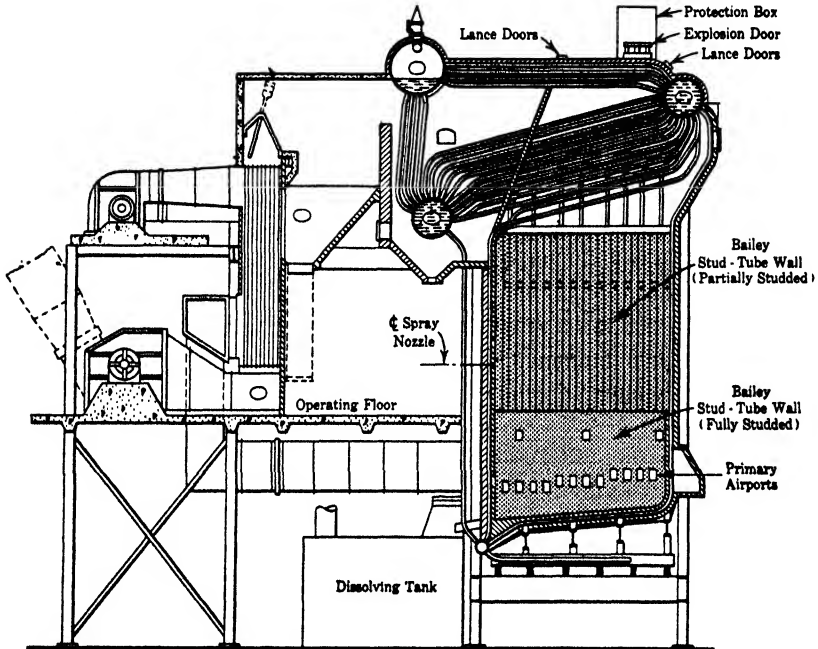
Courtesy Babcock and Wilcox Company

FIG. 18. TOMLINSON RECOVERY FURNACE.

distance of 4 to 5 feet below the level of the nozzle. Evaporation of the remaining water and partial charring take place until the accumulating mass breaks away and falls to the burning and smelting zone. Air for burning and smelting is supplied by ports under the deep bed of fuel thus formed, and produces a localized zone where reduction and smelting take place.

The liquor supplied to this furnace usually has a solid content of 55 to 60 per cent, but slight changes in liquor density have little effect on furnace operation. Should the liquor drop too low in strength, fuel oil can be fed with it. Salt cake may be mixed with the black liquor immediately before it enters the furnace; the nozzles will pass solid material up to $\frac{1}{4}$ inch in diameter, but large lumps must be absent.

When properly operated this furnace is capable of unusually high reduction, and with an efficient boiler it gives excellent steam production.

The operating technique of a modern recovery unit depends on its type and size, and differs materially from that of the old-type units. Its purposes are to recover the sodium salts from the black liquor in the form of smelt, reduce sodium sulfate to sulfide, and recover the heat of combustion of the organic matter in the form of steam. The importance of the last item may be seen from Gavit's estimate[20] that the total heat available in black liquor is sufficient to produce about 12,000 pounds of steam per ton of pulp, if it is handled in a properly designed recovery furnace and boiler.

The reduction of salt cake may be represented by the equation:

$$Na_2SO_4 + 4C = Na_2S + 4CO$$
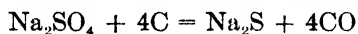
but it is obvious that no single equation can account for all the reactions taking place in the smelter. The reaction indicated does not go to completion, because some of the sulfide is oxidized to sulfate by the air blast, but with good operation 92 to 95 per cent of the sulfate is changed to sulfide and occasionally reductions of over 98 per cent are observed. The more intimately the liquor and salt cake become mixed the more complete the reduction.

The composition of various samples of smelt is given in Table 16.

TABLE 16

Sample	Na_2CO_3	NaOH	Na_2S	Na_2SO_3	Na_2SO_4	Insoluble
A	64.9	0.6	20.4	1.1	6.7	2.6
B	69.6	0.8	21.4	nil	5.1	2.4
C	70.0	1.1	20 0	0.7	0.8	3.2

In actual furnace operation a large quantity of soda is distilled off at a temperature far below the boiling point of any of the constituents except the hydroxide and chloride; such losses run from 50 to 150 pounds per ton of pulp. According to Schacht[54] the volatile material was about 85.5 per cent Na_2SO_4. Liander[38] discusses furnace reactions and concludes that the reversible reaction:

$$Na_2CO_3 \rightleftharpoons Na_2O + CO_2$$

goes to the right with an increase in temperature but is inhibited by any appreciable amount of CO_2. He feels that most of the sodium sulfate found in the stack gases is due to the union of sodium oxide with

the sulfur dioxide formed from organic sulfur and oxygen, and assumes the reaction to take place in three stages:

$$Na_2O + CO_2 = Na_2CO_3$$

$$Na_2CO_3 + SO_2 = Na_2SO_3 + CO_2$$

$$Na_2SO_3 + \tfrac{1}{2}O_2 = Na_2SO_4$$
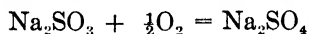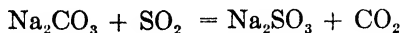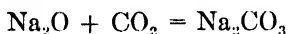
As these reactions take place in the boiler tubes, heat may be absorbed so rapidly that carbonate and sulfite may be obtained as flue dust. He considers 1150° C. a critical temperature above which volatilization increases rapidly.

It has also been considered possible that the boiling line of the system, Na_2S-Na_2CO_3, may dip to temperatures much lower than the boiling point of either constituent and thus at certain proportions give higher losses. No satisfactory diagram of this system is available.

A great deal of effort has been spent in trying to scrub the soda salts from the flue gases. The old rotary with a mass of loosely hung chain loops in the exit end, followed by disk evaporators, was probably the most successful of ·these scrubbers. Spray towers furnished with modern recovery units have for the most part removed only 10 to 15 per cent of the total dust. Combinations of spray and impingement towers have been slightly more successful. The removal of a large part of the chemical dust from a recovery stack by scrubbing with alkaline liquor offers promise, but is made difficult by the fact that the average particle size of the dust is of the order of 1 micron. The real chance for saving is to control furnace conditions so that volatilization and carry-over are at a minimum.

The Cottrell precipitator is frequently installed to collect sodium salts from the stack gases. This apparatus was originally a high tower filled with closely spaced vertical metal plates. A high-tension electric current passing from plate to plate charges the particles in the gas, which causes them to adhere to the plates. Owing to the difficulty of stoppage, a wet system was developed in which salts were continuously or intermittently washed from the electrodes. This was very successful with soda process recovery, but with the sulfate process the life was short due to excessive corrosion. The problem appears to have been solved by returning to the dry type and using wires instead of plates. · At such intervals as the wires become coated the current is reversed and the collected dust allowed to drop into hoppers below. While 95 to 98 per cent recovery of dust particles is possible, it is not considered economical to design for over 93 per cent recovery.

While it has been considered that sulfidity of the smelt is fixed by the alkali losses in the plant, the advantages of controlling pulp properties by the sulfidity content of the cooking liquor are obvious. Several methods are available to raise sulfidity without increasing the inventory of sodium salts. The earliest attempt at this was with niter cake which gives:

$$2NaHSO_4 + Na_2CO_3 + 4C = 2Na_2S + 4CO + CO_2 + H_2O$$
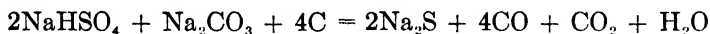
This reaction must be carried to completion in the furnace, as free $NaHSO_4$ in the dissolver gives off hydrogen sulfide and is likely to cause dangerous and costly explosions.

The addition of sulfur or sulfur dioxide to the black liquor before burning raises the sulfidity. The addition of sulfur is accompanied by high sulfur dioxide content of the flue gases, and unless this is scrubbed out with alkaline liquors it will be lost. If sulfur dioxide is added, sodium sulfite is formed in the black liquor and this reduces as completely as the sulfate. The use of sulfur through the blow pipes of the Tomlinson furnace is successful if a deep bed is maintained and the sulfur blown under this bed.

Savell[53] discusses the use of a mixture of sulfur and soda ash in proper proportions to substitute for salt cake. The intimate mixture of these two materials, such as is obtained by melting the sulfur into the soda ash, gives a product which is claimed to be a complete substitute for any ordinary commercial salt cake. It possesses the advantage of being converted in large part to sulfide and requiring less energy to complete the reduction. On heating to furnace temperatures the following reaction takes place:

$$3Na_2CO_3 + 3S = 2Na_2S + Na_2SO_3 + 3CO_2$$

Another novel method of sulfate mill make-up is to mix the waste liquor from a soda-base sulfite mill with the black liquor to replace both soda and sulfur. As an excess of sulfur dioxide is present, this will tend to give a high sulfidity unless soda ash is also added.

Stevens[57] suggests the use of gypsum, or salt cake containing it. This was probably used years prior to this reference, as the older pulp men in the South suggested its use with soda ash whenever a price advance in salt cake threatened. The conversion of the sulfur in gypsum, or anhydrite, to sodium sulfide takes place as follows:

$$CaSO_4 + 4C = CaS + 4CO$$
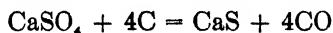
When this molten calcium sulfide-sodium carbonate mixture is dis-

solved in the green liquor it reacts to form sodium sulfide:

$$CaS + Na_2CO_3 = Na_2S + CaCO_3$$
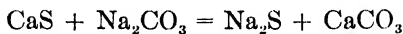
This has the disadvantage of making necessary the settling or filtering out of large quantities of lime sludge. As both CaO and CaS are non-volatile, there is no such loss as with soda compounds.

When it is desired to reduce sulfidity the use of soda ash in the green liquor is obvious. Waste liquor from nearby Rayon plants is sometimes used.

Green Liquor. From the smelting furnace the smelt flows in a red-hot stream through a water-cooled iron or stainless-steel spout to a dissolving tank containing water or dilute washings from the lime sludge in the causticizing room. When the solution has reached the desired density it is discharged into the causticizing system. The solution is usually tinted green from ferrous hydroxide, from which it is called " green liquor " to distinguish it from the " white liquor " obtained after causticizing. Good agitation or circulation of liquor in the dissolving tank will do much to prevent explosions caused by hydrogen sulfide or sudden generation of steam by the hot smelt.

Green liquor besides containing sodium carbonate and sulfide contains appreciable quantities of sulfate, thiosulfate, sulfite, aluminate, and silicate, and there is in suspension a quantity of slime or dregs. Lassenius[36] gives the following as limits of analysis of the slime:

	PER CENT
Insoluble inorganic	2.0– 4.0
Carbon	20.0–40.0
Fe_2O_3	8.8–20.4
Al_2O_3	1.6– 3.8
CaO	2.3– 5.7
MgO	2.0–11.8
SiO_2	2.5– 6.0
SO_4	– 6.2

In plants where green liquor or weak wash is used to scrub recovery stacks, an increase in thiosulfate, sulfate, and sulfite may be expected. When free sulfur is added to the furnace or dissolver a high polysulfide content is usually encountered.

The gases from the recovery furnaces have been analyzed by Klason[30] and found to contain 13 mg. of methyl mercaptan and 4 mg. of hydrogen sulfide per cubic meter. Hägglund and Hedlund[26] in an effort to check these data found 0.2 mg. of mercaptan and 550 mg. of hydrogen sulfide per cubic meter. In many modern furnace stacks the content of both chemicals is low or, under good conditions, absent.

Causticizing. The causticizing of soda ash by lime according to the equation:

$$Na_2CO_3 + Ca(OH)_2 \rightleftharpoons 2NaOH + CaCO_3$$
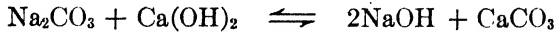
is one of the simplest chemical reactions, but in its application to the " green liquor " of the sulfate process there are so many factors which affect its progress that it becomes quite complicated.

The simplest equipment for carrying out this reaction consists of an agitated causticizing tank where the green liquor and quicklime are mixed and allowed to react. When the reaction is complete the agitation is stopped, the sludge allowed to settle for 3 to 8 hours, or until the mud has formed a compact layer in the bottom, and the liquor is decanted by means of a swing pipe decanter. The tank is then filled with water or weak wash, agitated, allowed to settle again and the wash water decanted as before. As many as four or five washes are sometimes given, but in modern batch systems there is usually one wash and the mud is then washed on a rotary filter. Sometimes separate tanks are used for causticizing and settling. If the lime is to be reburned, the incoming green liquor is either settled or filtered to remove dregs.

In recently designed mills the trend is toward continuous causticizing. The early Glamorgan system is being replaced by others, as the Swenson, the International Filter, or the Dorr systems. Among the advantages claimed for continuous operation are the saving of a considerable quantity of steam, floor space, operating labor, and alkali through uniformity of operation. The disadvantages are the tendency on the part of the operators not to get maximum causticity and clear liquor. Kress and Harrison[32] have shown that lime mud suspended in the cooking liquor causes a gray color in the fiber and a loss in strength.

The Dorr system of continuous causticizing is illustrated in the plan shown in Fig. 19, which is at present the approved layout for sulfate pulp mills which reburn the washed lime mud. For soda pulp mills the layout is identical except that the green liquor clarifier and the dregs washer are not used. This method, as illustrated in the flowsheet, Fig. 20, may be divided into four chief parts — lime slaking, recausticizing, mud washing, and lime reburning.

Where reburning is practiced the recovered lime and new lime are stored in two bins, each equipped with a mechanical feeder to charge them in proper proportions into a rotary lime slaker. Soda solution flows at a uniform rate through a tubular heater into the slaker and on into the Dorr bowl classifier which follows, and in which sand and unburned cores of lime are collected and thoroughly washed before being discharged to waste. The grit-free milk of lime overflows the

classifier and enters the first of three causticizing agitators arranged in series. These are insulated to conserve heat and are of such a total

Fig. 19.

volume that the slurry is retained for about an hour at a temperature of 85–90° C., thus assuring a high degree of conversion to caustic soda.

The discharge from the last agitator flows by gravity into the first thickener, in which the lime mud settles to the bottom and is moved to

PLANT FLOWSHEET
OF
DORR CONTINUOUS RECAUSTICIZING SYSTEM
AT UNION BAG & PAPER CORPORATION, SAVANNAH, GA.

SMELT DISSOLVER

DORR DREGS WASHER

NEW AND REBURNED LIME

DORR GREEN LIQUOR CLARIFIER

DREGS WASTE

Courtesy The Dorr Company

ROTARY LIME SLAKER

GRIT WASTE

WASH WATER

DORR BOWL CLASSIFIER

WASH WATER

OLIVER CONTINUOUS FILTER

DORR CAUSTICIZERS

WATER

WATER

WEAK LIQUOR

ROTARY LIME KILN

REBURNED LIME

DORR LIME MUD CLARIFIER

WHITE LIQUOR TO DIGESTER

DORR WHITE LIQUOR CLARIFIER

FIG. 20.

the center by slowly revolving rakes, while the clear caustic solution overflows to storage for use in the digesters. The lime mud is removed from the center of the thickener by a diaphragm pump, mixed with

weak liquor from the filter, and passed into a second thickener. From this the overflow goes to the weak liquor storage tank and the sludge to continuous vacuum filters, which discharge the dewatered mud as a relatively firm cake, directly into the lime kiln.

Chemical control for such a plant is centered at the following four points:

1. Strength of cooking liquor: regulated by the volume of wash water added from the constant head tank.

2. Rate of production of cooking liquor: regulated by the volume of soda solution added from the constant head tank.

3. Causticity or conversion: regulated by adjustable mechanical feeders under the lime bins.

4. Density of lime mud discharged: regulated by eccentric adjustment on Dorrco pumps.

Studies of the variables in causticizing have been made by Overwien,[49] Linder,[39] Goodwin,[22] and Lassenius.[36] The completeness of the reaction and the settling of the resulting mud are affected by concentration, temperature, sulfidity, and the quality of the lime and the method of slaking it.

At higher liquor concentration a lower causticity is reached with a certain amount of lime. Increased OH-ion concentration pushes the reaction toward the left and retards causticizing. Thus as sodium sulfide hydrolyzes,

$$Na_2S + H_2O \longrightarrow NaOH + NaHS$$
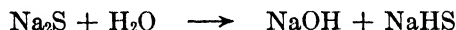
Increasing the sulfidity increases the concentration of OH-ion and hence limits the completeness of the reaction. Thus the causticity of liquor from the soda process is in general higher than from sulfate liquor. For a given alkali a higher sulfide also means a decreased carbonate content and hence less lime per ton of pulp.

With rising temperature the reaction speeds up and reaches equilibrium quickly. High temperature also induces rapid settling, but at the same time the solubility of $Ca(OH)_2$ drops and that of $CaCO_3$ rises, thus tending to throw the reaction to the left and lower the causticity obtained. A green liquor temperature of $190°$ F. appears to give a good balance of conditions in plant practice.

The method of slaking appears to have a marked influence on the settling of the resulting mud. Dorr and Bull[17] state that if 120 grams of lime is slaked (a) in 500 cc. of water, or (b) in 80 cc. which is then diluted to 500 cc., the latter gives, on causticizing, 12 times greater rapidity of sedimentation. It is therefore an advantage to slake the

lime in a small amount of liquid. They also obtained extremely high sedimentation velocities by slaking the lime with soda solutions and therefore recommend using green liquor for slaking the lime.

The principal quality of lime affecting good causticizing is rate of slaking. A good causticizing lime is one that slakes rapidly to form a crystalline, rapidly settling milk. This means complete use of the lime and the formation of fast-settling sludge. The lime should have as high an amount of active CaO as possible and should be low in magnesia, iron, silica, alumina, and sulfates.

The washing of the lime mud and the recovery of the sodium salts removed greatly affect the economies of the causticizing system. Rodowski and Knowles[51] give a complete analysis of actual losses totaling 26 pounds of salt cake per ton of pulp in a continuous causticizing system. Lassenius claims much lower losses in Scandinavian mills.

Wegscheider[61] blames the loss of sodium salts on the formation of insoluble double salts, $CaNa_2(CO_3)_2 \cdot 5H_2O$ and $CaNa_2(CO_3)_2 \cdot 2H_2O$. These can be broken up by water and washed out of the sludge almost completely by repeated rubbing and washing. Linder[39] states that they cannot be washed out profitably in the plant.

When it is desirable to increase the settling rate of the mud, because of lack of capacity or poorly settling liquor, the use of pearl starch is resorted to. This is added at the rate of 1 or 2 pounds per 1000 gallons of green liquor. Its action appears to be that of a flocculating agent. When it is desired to increase the settling of green liquor slime prior to causticizing, a small quantity of lime mud is added. Sometimes 4 or 5 pounds of crude animal glue per 1000 gallons is used, but it is not so effective as lime mud.

The lime sludge produced by causticizing was originally a waste product, but most plants today reburn the lime sludge and re-use the quicklime produced. A modern recausticizing plant should require less than 10 per cent of new lime. Although most lime sludges today are reburned in rotary kilns, the tray-type furnace such as the Bethlehem-Wedge and the Nichols-Herreshoff have been installed in some instances. No lime-reburning kiln is particularly efficient from a thermal standpoint, but the hearth type, though giving some mechanical difficulties, apparently produces a slightly higher grade of reburned lime at a somewhat lower fuel cost.

By-Products. The common by-products of the sulfate process are turpentine and tallol. From woods rich in turpentine and rosin, the former can be obtained without difficulty in the relief gases from the digesters. As thus recovered the crude turpentine is a vile-smelling liquid ranging from 50 to 90 per cent turpentine. The remainder con-

sists of pine oil, dimethyl sulfide, methyl mercaptan with some methanol, acetone, etc. Simple fractional distillation brings the mixture to a high degree of purity, but the sulfur compounds are persistent, and in order to obtain a product of satisfactory odor, chemical treatment is resorted to. This treatment employs lead acetate, sulfuric acid, hypochlorite, ethylene diamine,[21] caustic soda, and other chemicals, in addition to one or two fractionations. The product consists chiefly of alpha-pinene; it must be labeled " sulfate wood turpentine " and must conform to specified limits as to sulfur and chlorine content.

According to Blengsli[8] the turpentine possible of production in the sulfate industry is about 11,000,000 gallons of the crude material, but in 1938 only 2,000,000 gallons were recovered.

The resins and fats in the wood combine with the alkali to form soaps which tend to separate on cooling or concentration. In addition to the sodium salts of resin and fatty acids this soap contains an appreciable amount of phytosterol. When treated with an acid, such as sulfuric or sulfur dioxide, a dark, oily liquid separates, which is known as tallol. According to Blengsli this averages 45 per cent fatty acids, 45 per cent rosin acids, and 10 per cent unsaponifiable material containing 30 to 40 per cent of phytosterols. The resin acids are abietic and its isomers; the fatty acids are mainly oleic and linoleic, with a little linolenic and stearic. This material finds use in soaps, in greases, and as an emulsifying agent. It may be purified with chemicals, such as hydrogen peroxide, bleached to some extent by fuller's earth, or distilled under vacuum to produce a higher-grade product. Numerous patents on its treatment have been granted, and a number of plants in this country and abroad produce it in one of its various forms. The economics of its recovery as a by-product as compared with burning the original soap depend on conditions in each particular plant.

Other possible by-products are acetic and formic acids, tars and oils from the black liquor; and it has been proposed to isolate saccharinic and related acids from this liquor, but no commercial use exists at present. Sulfate lignin contains more or less sulfur, which makes its utilization doubtful.

It should be remembered that fuel is one of the principal raw materials in the manufacture of pulp, and that the increasing efficiency of heat recovery from modern recovery furnaces and boilers gives a fuel value to the black liquor which will necessitate the recovery of a considerable value in by-products to make it economical to divert.

Materials of Construction. In the early mills iron or steel was the standard material, but corrosion problems varied widely as to cause and

characteristics and as new alloys were developed the sulfate mills were among the first to take advantage of them. Salt cake is often acid, as are also the recovery flue gases and evaporator vapors, while the green, white, and black liquors are strongly alkaline. Alkali containing chlorides and thiosulfates attacks steel when hot, and sodium sulfide attacks copper, zinc, aluminum, and iron oxide. Benedicks[5] describes a rather unusual worm-hole action in digester heater tubes, and this phenomenon has been observed in other pieces of equipment where hot liquor is present.

McGregor[42] gives the detailed results of tests of a large number of ferrous and non-ferrous alloys in five different positions in the system as follows: (a) in No. 1 effect in the evaporator containing sulfate black liquor at 30° to 33° Bé. and 100° F.; (b) in cooking liquor containing about 150 grams per liter of NaOH and 40 grams per liter of Na_2S; (c) in sulfate green liquor with 50 NaOH, 80 Na_2CO_3, and 80 Na_2S; (d) in alkaline hot water tanks; and (e) in bleach liquor. Lee[37] gives a review of materials used to combat corrosion in 25 sulfate mills; though no definite conclusions can be drawn there is certainly a preference for alloy steels and monel metal.

The use of the more expensive metals is confined to pumps, agitators, filter wires, valves, and other moving parts. Castings and tubes of 18-8 stainless are preferred for alkaline liquors; machined parts are usually made of 18-8s, and 18-8smo is used for acid resistance or where welding in the field is desired. For the last application 18-8scb is coming into use. Monel is used for acids or mild alkalies, or where a great deal of wear and stress is encountered. Pump rods, caustic mud filter wires, and incinerator and lime kiln castings of this material give unusual service.

For evaporator tubes 3–6 per cent nickel and 3–6 per cent chrome steels are coming into use. In evaporators it is said[2] that liquor-side corrosion is most frequent if the liquor is above 220° F. and the concentration of soda above 40 per cent. The higher the sulfidity, the greater the corrosion. With 25 per cent sulfidity the average life of 10-gage steel tubes is 13 months, with failure usually 6 to 8 inches from the top. Alloy 18-8 is too expensive, but 5 per cent nickel steel will probably last four times as long as mild steel.

The early recovery furnaces were usually constructed of soapstone blocks, but later magnesite and chrome bricks were used. At the present time plastic chrome ore is used to make monolithic linings which have many times the life of the older materials. It is important that proper precautions be taken to insure steam relief and proper reinforcement on drying.

The real solution to any mill corrosion problem is to experiment with materials for each application and keep accurate records. Many metals that resist corrosion scale badly or promote corrosion in nearby dissimilar metals by galvanic action, whereas in other applications erosion plays the major part and corrosion is secondary.

Life of Sulfate Mill Equipment.   Since the use of mechanical equipment is rather closely related to the chemistry of the process an estimate of its probable life and cost of annual repairs may be of interest. Accurate records of this sort are seldom available, and the problem is complicated by the fact that equipment often becomes obsolete and is discarded before it is worn out.   Moreover the same machine may vary considerably in life under different conditions of care and treatment in different mills, so Table 17 must be considered as an expression of opinion rather than a collection of definite facts.

TABLE   17

Equipment	Probable Life	Cost of Annual Repairs
	Years	Per cent
Chippers..................................	10–12	10
Re-chippers.............................	10	15
Conveyors................................	15	10
Chip screens — shaker....................	12–15	15
Chip screens — rotary	20–25	5
Digesters, including equipment..............	15–20	10
Storage tanks............................	30	1
Diffusers.................................	20	10
Stock chest.............................	50	2
Stock pumps, including lines...............	10	5
Screens — centrifugal.....................	20	8
Knotter screens — rotary	25	5
Wet machines............................	15	5
Rotary furnaces..........................	25	10
Smelters.................................	1¼	10
Dissolving tanks.........................	10	5
Causticizing tanks........................	3	5
Settling tanks............................	25	2
Pumps...................................	5	10
Evaporators.............................	10–15	15
Storage tanks............................	30	1

Analytical Methods.   The methods for the analysis of the liquor in the sulfate process are more complicated than for similar products in

the soda process. The following procedure for white and green liquor is a modification of one worked out by the Forest Products Laboratory.

(a) *Total Alkali.* Two cubic centimeters of the liquor are titrated with 0.5 N acid using methyl orange as an indicator. This gives the acid equivalent to the Na_2CO_3, NaOH, Na_2S, and $\frac{1}{2}Na_2SO_3$.

(b) NaOH + Na_2S. To 2 cc. of the solution contained in a 100-cc. flask add 20 cc. of a 10 per cent solution of $BaCl_2$ (more for green liquor) and make up to the mark with boiling distilled water; shake thoroughly and allow to settle; cool and draw off 50 cc. of the clear liquid and titrate with 0.5 N acid, using methyl orange as indicator.

(c) Na_2S + $Na_2S_2O_3$ + Na_2SO_3. Find by trial the approximate amount of standard iodine necessary to react with 2 cc. of the liquor. Taking about $\frac{1}{2}$ cc. less than this amount of iodine in 200 cc. of water, add 2 cc. of the liquor, acidify with acetic acid, and complete the titration using starch as an indicator.

(d) $Na_2S_2O_3$ + Na_2SO_3. Five cubic centimeters of liquor are pipetted into a 250-cc. volumetric flask, 15 cc. of a 5 per cent solution of alkaline zinc chloride (made up by adding NaOH to a $ZnCl_2$ solution in sufficient amount to redissolve the precipitate formed) are added, and the solution is made up to the mark and filtered through a double thickness of dry filter paper. Fifty cubic centimeters of the clear filtrate are pipetted into an Erlenmeyer flask, 2 drops of methyl orange are added, and the mixture is acidified with HCl. The solution is then brought back with strong NaOH and then 0.1 N NaOH to a point just on the acid side of the neutral point. Two drops of methyl orange are added to a clean Erlenmeyer flask and made up to about the same level as the titration sample with distilled water. Tenth normal HCl is then added to the blank sample until a color which matches that of the titration sample is obtained. This is saved for comparison. The original solution is then titrated with 0.1 N iodine, using starch indicator. This titration yields the sulfite and thiosulfate together. The blue starch color is dispersed with a drop of thiosulfate, and the solution is titrated back to the methyl orange standard with 0.1 N NaOH. The number of cubic centimeters multiplied by 0.0042 gives the amount of Na_2SO_3 in the sample, and this figure divided by 0.0063 gives the iodine value of the sodium sulfite. Subtract this from the iodine titration previously obtained, which will give the iodine equivalent to the sodium thiosulfate present.

Calculations:

c–d gives the cc. of iodine for sodium sulfide

a–b gives the cc. for Na_2CO_3 and $\frac{1}{2}Na_2SO_3$

The titration in (b) expressed as Na_2O minus the sodium sulfide as Na_2O gives the Na_2O equivalent to the NaOH present.

This does not include the determination of Na_2SO_4, which may be accomplished by acidulating a measured volume of the solution with HCl, boiling until all H_2S is driven off, and then precipitating the sulfate with $BaCl_2$. The $BaSO_4$ is filtered off, washed, ignited, and weighed, and from this weight the Na_2SO_4 may be calculated.

Moe[44] uses a silver nitrate solution containing 87.89 grams $AgNO_3$ per liter for determining sulfides. When 1 cc. is titrated the number of cubic centimeters of $AgNO_3$ used represents pounds of Na_2S per cubic foot of liquor. He gets the end point directly in the solution by shaking to coagulate the silver sulfide and noting the point at which no further precipitate is formed by a drop of the reagent. Oliver[48] improves on this by the use of ammoniacal silver nitrate. This reagent can best be used by titrating approximately 10 cc. of liquor in a large beaker and swirling over a white paper as titration proceeds. At the end point a drop of solution gives a clear spot rather than a cloudy one.

The sulfide in black liquor may be determined by titrating with ammoniacal zinc nitrate, using an ammoniacal nickel salt as an outside indicator on a spot plate.

For total soda in either liquor or smelt the zinc uranyl acetate method[13] is the most desirable. A refrigerator is a decided advantage for speed with this method.

Mercaptans in turpentine or an organic solvent may be determined by titration with a mineral spirits solution of copper oleate. The green solution turns yellow as long as mercaptan is present but is colored green with a few drops of titrating solution at the end point. Mercaptans in gases may be collected in turpentine or gasoline by bubbling through an absorption apparatus and then titrating.

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CHAPTER V

THE SODA PROCESS

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Many of the operations in the soda process are similar to those in the sulfate process, but it is the older and simpler of the two and is more easy to study in detail.. Moreover, the sulfate pulp industry is growing rapidly in importance, while the soda process has changed and expanded very little for a good many years. It has therefore been attempted to place the general descriptive matter in the preceding chapter and include here those features in which the soda process differs from the sulfate, or in which its simpler nature has made more detailed studies possible.

The principles upon which the process depends are the solvent power of the caustic soda for certain constituents of the wood, and the hydrolysis of other constituents, resulting to a considerable extent in the formation of products of an acid nature which are then brought into solution as salts of soda. Both these processes neutralize the alkali and make it useless for further work until it is regenerated. The reactions and decompositions involved are complicated and ill-defined, and are still not well understood. The degradation of the woody constituents is, in general, far greater than for the same constituents when dissolved by the sulfite process. Because of this, a study of the end products shows little about the method of attack on the woody matter, and as a matter of fact few definite compounds have been isolated from the black liquor. It has been proved that there is a considerable amount of combined acetic acid and a small amount of formic acid,[1] and the acetic, at least, is probably produced by attack on the methoxyl groups of the lignin. Furfural has been shown to be absent, and reducing sugars are either absent or present in traces only. Fatty acids and resins are saponified and dissolved, but they are present in such small amounts that they play a very minor part in the cooking process.

Even at low temperatures alkali dissolves a very appreciable proportion of the non-cellulose constituents of the wood, and if the temperature is raised the action is greatly intensified. Experiments on small poplar chips showed that a 3.3 per cent solution of caustic soda would dissolve 20.3 per cent of their weight by 24 hours' treatment at 25° C.,

and if the temperature was raised to 80° C. the wood lost 31.6 per cent of its weight in the same time. Higher temperatures, such as are obtained by steaming under pressure, still further enhance the solvent power of the alkali and the speed with which it acts.

In working with materials other than wood, due consideration must be given to pectous substances. In his work with bamboo Raitt[24] found that pectose (matter soluble in 1 per cent NaOH solution at 100°) gelatinized at the temperatures employed in digestion and was therefore likely to become mechanically attached to the cellulose and very difficult to wash out. Pectose, fat, and wax, grouped together, neutralize 0.32 per cent of NaOH for each 1 per cent of these substances found in the raw material. Lignin, unlike pectose, is not soluble in weak solutions or at temperatures below 130°.

Wood Used. The wood used in the soda process was at first chiefly poplar, but because of its increasing cost and scarcity other woods are now frequently substituted. Among these may be mentioned basswood, maple, birch, cottonwood, yellow poplar, sycamore, buckeye, beech, gum, and chestnut. Since the northern hardwoods, such as beech, birch, and maple, have come into more general use it has been found that they have certain advantages over poplar. Beech and maple are less subject to decay and can therefore be kept longer in storage with less loss from rotten wood. Because of their greater density the yield per cord is greater and also that from a digester charge. On the other hand the logs are too dense to be driven in streams, and they wear out the chipper equipment rapidly; some woods are even so dense and cross grained that they cannot be split with the usual equipment, but have to be sawed. Another disadvantage is the presence of resins or fatty acids which are likely to combine with the lime salts during the cooking or bleaching operations and cause much trouble from " pitch " spots.

The behavior of hardwood chips in the digester is somewhat different from that of poplar. During an idle period of short duration it is safe to fill a digester with dry poplar chips, but not with hardwood, because hardwood chips settle so solidly that they do not steam and cook normally, both temperature and pressure being low and necessitating additional time for the cook. Hardwood cooks are likely to blow less completely than poplar and reblowing is more often necessary in order to get all the fiber out of the digester.

It used to be believed that if poplar and hardwoods were cooked together the poplar would be overcooked and both yield and strength lost. More recent studies have proved that both kinds of wood require the same percentage of caustic soda, based on the dry weight of the

wood, and that they cook in the same time and at the same pressure. Moreover, the best available figures show that cooks of mixed woods give very nearly the yields and strength tests which would be expected from an average of the figures for separate cooks. These laboratory results have been checked by large-scale operations which showed that, when mixed woods were cooked together under the conditions of time, pressure, and percentage of caustic soda usually applied to poplar cooks, the fiber bleached readily, was free from shives, and was of a strength intermediate between that of poplar and hardwood fibers.

In a mill which uses both kinds of wood, mixed cooking would have certain advantages. The pulp delivered to the bleach plant would have a more uniform bleach requirement than if the kinds of pulp alternated and it would be much easier to maintain uniformity of color and strength. It would also result in uniform cooking conditions in all digesters and permit a schedule of evenly spaced blows, with consequent equalization of boiler-house load, better waste-heat utilization, etc. The chief difficulty would be in supplying a uniform mixture of woods, which is very essential, for the different kinds vary to a considerable extent in weight per cord and the caustic soda added must be based on the weight of the wood and not on the number of cords. Since the strength of fiber varies in the different woods a uniform mixture would also go far toward eliminating variations in the strength of the fiber produced.

For long-fibered stock, spruce, hemlock, pine, and fir are sometimes cooked by the soda process. They require more alkali and longer cooking and yield less pulp than the broad-leaved woods. With single-stage bleaching it is almost impossible to obtain a good white color without greatly overcooking the wood, but much better color and strength can be obtained with modern multistage bleaching. According to the United States Department of Commerce[31] the kinds and amounts of wood used in the soda process in 1930 and 1936, as compared with those for 1926, are as shown in Table 18.

Preparing the Wood. On account of the vigorous action of the alkaline solutions less care is necessary in preparing the wood than for the sulfite process. Knots are either dissolved by the treatment or left in such a condition that they are easily separated by the screens. Contrary to the usual belief the inner bark is a source of trouble and should be removed as completely as possible. It cooks with difficulty, uses up fully as much caustic soda as sound wood, and bleaches far less readily. If wood and inner bark are cooked together the resulting product is liable to be contaminated with brown, stringy shives. The outer bark also uses up a large amount of caustic soda and in cooking

breaks down into masses of cells which will not bleach to better than a yellowish brown color and hence cause dirt specks in the finished pulp. These are not the only faults of bark, for its rough surface tends to catch such dirt as cinders and sand, and transfer it to the pulp.

TABLE 18

Wood	Cords Used in		
	1936	1930	1926
Spruce..............................	16	22,610	40,180
Hemlock............................	912	1,357	....
Yellow pine, southern................	37,745	79,957	104,197
Balsam fir..........................	560	3,754	....
Poplar.............................	381,089	402,230	396,610
Chestnut...........................	....	69,724	....
Yellow poplar.......................	91,818	107,185	134,297
Birch, beech, maple..................	47,843	57,317	....
Gum................................	22,169	38,475	49,699
Other woods........................	155,660	49,592	173,617*
Slabs and mill waste.................	12,061	18,028	2,200
Jack pine...........................	19,819	....	....
Cottonwood.........................	26,289	....	....
	795,981	850,229	900,800

* Includes basswood, beech, birch, maple, buckeye, cedar, chestnut, cottonwood, Douglas fir, willow, and white pine.

It is desirable, though not absolutely necessary, that decayed portions of the wood be removed. In general, decayed wood is completely resolved during cooking, but it uses up much more soda than sound wood and gives a greatly reduced yield of fiber which is very hard to bleach and goes to pieces very rapidly in the beaters. The cellulose in partly decayed poplar wood was found to be 24.9 and 27.0 per cent in two samples, as compared with 63 per cent for sound wood. Since there is no simple and accurate way to measure the degree of decay of chips any statement regarding its effect is subject to serious errors, but experiments with birch wood have indicated that each 1 per cent of decayed wood in the digester charge increases the cost of the fiber produced by about 50 cents per ton.

The chipping and screening of the chips preparatory to charging the digester follow the usual methods as described in Chapter IV. The length of chips when poplar is used is about ¾ to 1¼ inch.

Digesters. In the early days of the soda process rotary digesters were used, but as engineering practice advanced they were replaced by

vertical stationary types because of the saving in floor space required, and especially on account of the shorter time for filling and emptying. This is a very appreciable item, as a rotary holding 3 to $3\frac{1}{2}$ cords requires 3 hours for blowing down pressure, discharging the contents, and refilling with chips and liquor, whereas a vertical digester of 3250-cu.-ft. capacity and holding 14 to 15 cords needs only 1 hour for the equivalent operations. The size of vertical digesters varies considerably, the larger ones being usually of more recent installation; diameters range between 7 and 12 feet, and heights between 27 and 50 feet. A digester 30 by 8 feet will hold about 5.5 cords, while one 49 by 10 feet will have a capacity of about 15 cords. When the chips are fed by gravity and the liquor run in at the same time, it has been estimated that about 8.5 to 9.5 pounds of dry poplar chips, or 11.5 to 13.5 pounds for mixed hardwoods, will be contained for each cubic foot of rated capacity.

The only real advantage of the rotary digester was the very thorough mixing of the chips and liquor, and this can be obtained by some of the modern liquor circulating systems, either with or without the use of an external heater. Such indirect heating is more common in making sulfate pulp, but for soda fiber it has the same advantages of steam saving, return of condensed steam at high temperature and pressure to the boilers, and the possibility of starting the cook with a more dilute liquor.

As in the sulfate process the digesters are unlined steel or iron vessels. Older types were riveted, but welding is to be preferred because of the difficulty in making a riveted joint tight against alkaline solutions.

The time required to fill a 15-cord digester by gravity only is about 15 to 20 minutes. A tamping or distributing device is sometimes used to obtain a greater charge and more even distribution of the chips and thus insure more even circulation of the liquor during the cook. This may increase the digester capacity by as much as 15 per cent, and the only objection is the longer time required for filling. Although it is seldom done because of the expense and delay involved, it is very desirable to weigh the chips and sample them for moisture as they pass to the digesters. This gives a much better basis for estimating yields and also valuable information regarding the quality of the wood and the uniformity of the digester charges. A weightometer is sometimes applied to the conveyor supplying the chip bins to give over-all weights of chips used, but this accomplishes only part of the desired object.

Cooking Liquor and Its Preparation. The cooking liquor for the soda process consists of a solution of caustic soda containing a small amount of sodium carbonate; it is thus much less complicated than the sulfate cooking liquor, which contains at least two active constituents. The presence of carbonate is not desired, as it takes no part in

cooking, but it is unavoidable because the causticizing reaction between lime and soda ash does not go to completion.

Factors influencing causticizing are concentration, temperature, agitation, and method of slaking and quality of lime, as in the sulfate process. The influence of concentration is shown in the following figures.[18]

Liquor before Causticizing		Liquor after Causticizing
Per Cent Na₂CO₃	Specific Gravity	Per Cent Causticity
2	1.022 at 15° C.	99.4
5	1.052 at 15° C.	99.0
10	1.107 at 15° C.	97.2
14	1.150 at 15° C.	94.5
20	1.215 at 30° C.	90.7

It is obvious that the lower the concentration the higher the causticity and that a demand for a definite concentration sets a limit to the causticity attainable. Attempts to increase the causticity by boiling either under diminished or increased pressure have met with no success; practically all causticizing is therefore done in tanks under atmospheric pressure.

In the older batch process, where quicklime and soda ash solution are mixed and allowed to react, it has been proved that time of boiling and degree of agitation are to some extent interchangeable and that if agitation is vigorous enough the charge need not be heated above 85° C. Agitation by mechanical means is best; the use of compressed air is not recommended as it reduces the causticity in proportion to the amount of carbon dioxide in the air used. As a rule the heating and agitation should be continued for about an hour, but it is doubtful if the gain in causticity by carrying it beyond this time will pay for the extra expense.

The sequence of operations in batch causticizing soda liquor is practically the same as for sulfate liquor, except that a second boil with more soda ash is sometimes made to use up the excess lime added in the first boil.

Investigations of the causticizing operations on a laboratory scale by Harrop and Forrest[13] showed that excess of lime and increased time of boiling increased the conversion to caustic soda but decreased the rate of settling of the sludge. Slaking the lime before adding to the soda ash solution also greatly delayed settling. Dorr and Bull[8] have also investigated many of the conditions affecting causticizing and show that

the rate of settling decreases very greatly as the time of agitation increases. McKee and Chilton[19] studied the action of slaked lime in excess on sodium carbonate and silicate in mixtures. Under conditions which would give high causticity with carbonate alone, poor causticity resulted when silicate was present, but by allowing more time for the reaction good causticity resulted. The sludge, however, is more bulky, settles poorly, and requires more wash water to free it from caustic soda.

The rate of settling is a very important factor where the charge is settled in the reaction tanks and the clear liquor drawn off. It is greatly affected by the lime used; some limes give sludges which settle rapidly while others require much more time and never settle as densely. Proper selection of lime will usually assure reasonable freedom from settling troubles, though variations in the lime may cause occasional annoyance. Many plants avoid all such troubles by using continuous filters to separate the sludge from the liquor. These give clearer liquor than settling, and the loss of soda in the sludge is said to be considerably less than by the old methods. Their use also allows the direct causticizing of the black ash, without separation of the carbon by leaching, which cannot be done where settling methods are employed, because of the bulk of the carbon. Black ash is directly causticized in several plants without trouble from carbon in the cooking liquor, and the carbon in the sludge burns out completely during the recovery of the lime.

In modern plants it is common practice to prepare the caustic soda by continuous operations. Plants of this type have made their greatest advances in the sulfate process, and they are discussed in more detail in that chapter.

The lime mud produced in causticizing was formerly a waste product but more recently a number of uses for it have been developed. Very considerable quantities are employed in paint and rubber manufacture and the paper industry itself utilizes very large amounts as a filler or a coating pigment. All these uses necessitate special care in the causticizing operation in order to obtain the very fine-grained carbonate which is necessary for such work, and also in the subsequent washing operations in order to insure freedom from caustic soda and residual free lime.

Besides these uses a considerable number of plants recover the lime for re-use by burning the lime sludge in kilns as mentioned in Chapter IV. Table 19 shows the analyses of new lime and of that recovered from the lime sludge after its use. The lower quality of the product is obvious.

The strength of the caustic liquor used in cooking varies from 8° to 15° Bé. at 60° F., according to operating conditions. For a liquor pro-

TABLE 19

Component	New Lime	Reclaimed Lime
	Per cent	Per cent
Calcium carbonate, $CaCO_3$.............	4.48	3.91
Iron and alumina, Fe_2O_3 and Al_2O_3......	0.15	1.62
Silica, SiO_2.........................	0.16	0.70
Calcium oxide, CaO..................	92.00	89.58
Magnesia, MgO......................	2.62	1.96
Undetermined.......................	0.59	2.23

duced by continuous causticizing and not subsequently mixed with any electrolytic soda these strengths would correspond to approximately 0.45 to 0.85 pound per gallon of caustic soda with a causticity of about 91 per cent. Average conditions would be in the neighborhood of 0.65 pound per gallon, but this might have to be raised or lowered slightly to allow for very wet or very dry chips. If the digester is heated by an exchange heater this will permit a lower strength of cooking liquor to be used.

The volume of liquor added for each cord of wood in the digester varies quite widely in different mills and with the different kinds of wood being handled. Unless a higher concentration of alkali is employed for hardwood than for poplar the volume used for the hardwood must be greater in order to have the correct percentage of alkali present. The gallons per cord for poplar are known to be as high as 1100 and as low as 500. This latter figure is extremely low, and it doubtless caused a considerable loss in yield and a lowering of the strength of the fiber because it did not cover the chips sufficiently well to protect them and to give good circulation of the liquor. In this connection experiments have shown that absolutely dry poplar chips require a little over twice their weight of water to saturate them. If it is assumed that the chips contain 30 per cent moisture as they enter the digester they would require about 460 gallons of liquor per cord to complete this saturation, which would leave only 40 gallons per cord for circulation if not over 500 gallons per cord were used. Such small volumes as this are probably never used at present.

It is desirable, of course, to use as little as will give good results, because of the consequent low steam requirement and the decreased cost for evaporation in the recovery of the soda. These two points are not so important as formerly because of better thermal handling of the fiber and liquor after blowing and also the recovery of steam by separators and accumulators. A gain is also made by diluting the cooking

liquor with black liquor instead of water, thus enabling a stronger black liquor to be sent to the recovery plant.

Cooking. The cooking operation in the soda process is a relatively simple one, the object being to reach full pressure as quickly as possible and maintain it to the end of the cook. During this period the air

TABLE 20

Caustic Soda Used		Steam Pressure	Hours at Pressure	Yields Per Cent		Per Cent Bleach Required	Per Cent NaOH Consumed
Per Cent on Wood	Grams per Liter			Good Fiber	Screen-ings		
22	80	110	5	46.4	0.6	29.5	19.6
28	80	110	5	37.7	0.0	6.8	22.0
34	80	110	5	30.9	0.0	4.2	25.7
40	80	110	5	28.2	0.0	3–4	26.8
50	80	110	5	24.3	0.0	...	28.3
28	40	110	5	42.1	0.2	6.6	21.2
28	60	110	5	41.1	0.0	6.7	22.2
28	80	110	5	37.7	0.0	6.8	22.0
28	100	110	5	36.4	0.2	6.9	23.1
28	80	70	5	45.9	0.0	7.0	19.9
28	80	90	5	39.5	0.0	6.0	22.1
28	80	90	5	41.3	0.0	7.1	21.7
28	80	110	5	37.7	0.0	6.8	22.0
28	80	130	5	34.1	0.0	7.3	24.4
28	80	110	3	40.5	0.0	6.4	21.8
28	80	110	5	37.9	0.0	6.8	22.4
28	80	110	5	35.9	0.0	6.1	22.9
28	80	110	5	37.5	0.0	6.8	21.6
28	80	110	7	35.2	0.0	...	23.9
28	80	110	7	35.2	0.0	7.1	23.5
28	80	110	9	35.2	0.0	6.2	23.7
28	80	110	9	36.1	0.0	7.3	23.7

which collects in the top of the digester is blown off several times through the " relief pipe " so that no false pressure may be recorded on the gages. The uniformity of the cook depends on good circulation of the liquor, which in practice is obtained in several ways. Some of the older digesters are fitted with internal circulating pipes on the same principle as the vomiting pipes in rag boilers, but much the better way is to circulate by external pumps, either with or without passage through an exchange heater. Several modern systems of circulation are illustrated in Chapter IV. Such systems may entail the use of a

pump capable of throwing at least 1500 gallons per minute for a 15-cord cook, and assuming that it is working to capacity the entire volume of liquor added to the digester would be circulated every 10 minutes. Relatively little power is required for pumping, but it has been estimated that the expenditure of 40 hp. for a 15-cord digester is fully justified.

In spite of the apparent simplicity of the process there are a number of factors which greatly influence the results obtained, and their proper adjustment is essential for uniform and satisfactory cooking. Much study has been given to these factors, and the following discussion is based on two series of tests under somewhat different conditions. In

TABLE 21

Caustic Soda Used		Cooking Temperature, °C.	Hours at Pressure	Yield per Cent	Bleach Required	Per Cent NaOH Consumed
Per Cent on Wood	Grams per Liter					
16	36.4	175	4.25	55.4	13	12.6
18	41.0	175	4.25	53.5	10	13.3
20	45.5	175	4.25	51.2	8.4	14.2
22	50.0	175	4.25	49.4	7.0	15.3
26	59.1	175	4.25	47 0	7.0	....
30	68.2	175	4.25	43.0	5.0	19.6
22	50	160	4.25	56.0	12.0	12.6
22	50	165	4.25	53.5	9.0	13.0
22	50	170	4.25	51.8	8.0	14.4
22	50	175	4.25	49.4	7.0	15.3
22	50	180	4.25	47.2	6.5	15.3
22	50	175	3.00	50.8	7.8	14.5
22	50	175	4.25	49.4	7.0	15.3
22	50	175	5.50	48.0	6.6	16.6

the first the cooking was done in a small rotary digester heated externally with a burner, the cooks were made under rather severe conditions, and the fiber was bleached to a relatively low color in a single stage. In the second series a steam jacketed digester was used, less caustic was added, its concentration was lower, the time of cooking was less, and the fiber was bleached to a considerably higher white in a two-stage treatment, the first part of which was with chlorine. All experiments were made with poplar chips, and all data are figured on the bone-dry basis. Tables 20 and 21 give the data for these two series of experiments.

The data for yields as compared with the variable cooking factors in these two tables are collected graphically in Fig. 21; the effects of the variables on the bleaching properties of the fibers are shown in part in Fig. 22. Considering the yields, it is seen that they fall into two distinct groups according to the general severity of the cooking conditions. In both groups the same tendencies are shown, but the slightly different slope of the curves indicates that under more severe cooking conditions an increase in the severity of the variable causes a slightly greater loss in yield. It is evident that the percentage of caustic added is the factor having the greatest influence on the yield; the next in importance is the pressure at which the cook is made, while the hours of cooking and the strength of the caustic soda solution at the start of the cook have about the same influence, but less than that of steam pressure.

From the curves in Fig. 21 and from the data presented by the Forest Service[10] the change in each variable factor necessary to cause a decrease of 1 per cent in the yield has been calculated to be about as follows:

Decrease in Yield of 1 Per Cent Caused by	According to Experiments by		
	Severe Cooks	Light Cooks	U.S. Forest Service
Increase of NaOH used by	1.3 per cent	1.2 per cent	2.0 per cent
Increase of time by........	1.2 hours	0.9 pours	1.0 hours
Increase of steam pressure by....................	5.0 lb.	7.0 lb.	5.0 lb.
Increase of concentration by....................	10 grams per liter	....	13 grams per liter

Considering the decidedly different conditions in these groups of cooks the agreement among these figures is rather remarkable.

The two groups of severe and light cooks show differences in yields which lead to the conclusion that a part of the gain under light cooking conditions is due to the more complete covering of the chips because of the larger volume of cooking liquor, as well as the lower concentration of the caustic soda. It has been proved that the yields under light cooking conditions are much more nearly in line with those of semi-commercial cooks than are those in the gas-heated digester, and it is apparent that they more nearly duplicate those of large-scale, regular operations. There is also proof that the effect of steam pressure on yield is very nearly the same on a semi-commercial scale (400 pounds of chips) and in laboratory cooks.

The effect of the various cooking conditions on the bleach required is not so easily compared as the yields because the fiber from the two

series of tests was bleached in different ways and to different degrees
of whiteness. In the group of more severe cooks the factors of steam
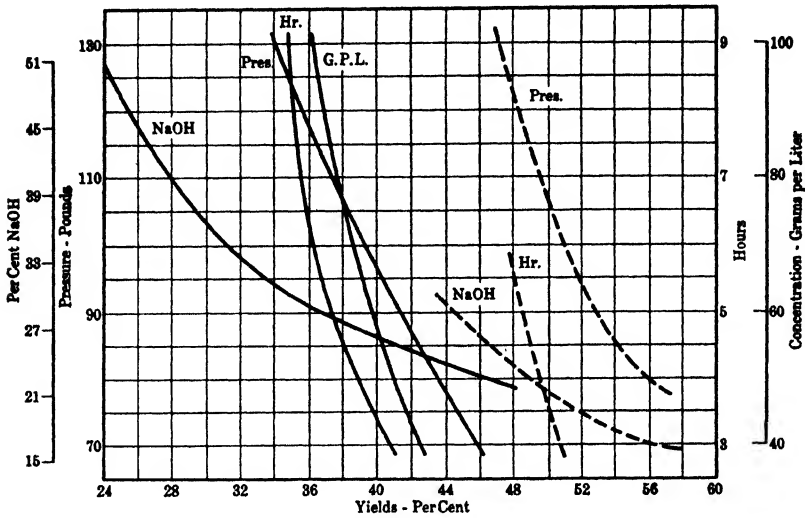
FIG. 21.   YIELDS *vs.* COOKING CONDITIONS IN SODA COOKS.
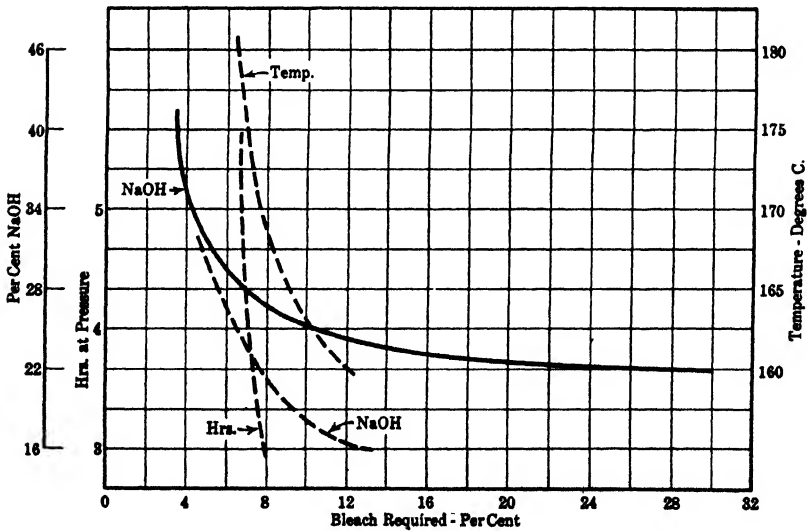
FIG. 22.   BLEACH REQUIRED *vs.* COOKING CONDITIONS.

pressure, concentration of caustic soda, and time of cooking have little
effect because of the very thorough cooking under even the least severe
of the conditions. For this reason the effect of these factors in this

group of cooks is not shown in Fig. 22. The variation in caustic soda used does cause a wide variation in the bleach required, as shown in the curve in Fig. 22. From this it is seen that 22 per cent of caustic gives practically unbleachable fiber, yet the same amount in the lightly cooked series produces fiber which bleaches readily. This, again, is doubtless due to the more complete covering of the chips with liquor in the latter cooks.

In the series of less severe cooks steam pressures between 75 and 130 pounds are seen to have a distinct influence on bleachability, while the time of cooking within the range studied is of much less importance. In this series it was not possible to separate the effects of caustic added and concentration of caustic soda, but their combined effect is sufficient to raise the bleach required from 5 to 13 per cent when the caustic used drops from 30 to 16 per cent.

Experiments on maple, beech, and white and yellow birch have shown that the curves for yield and bleach required *vs.* caustic soda employed and hours of cooking have practically the same slope as the curves for poplar treated under light cooking conditions, though the position of the curves on the charts may be quite different. The one exception to these statements is that at low percentages of caustic soda used the curves for bleach required do not rise so abruptly as those for poplar, indicating that more severe cooking of the hardwoods would still further reduce the bleach required by the fiber.

Davis[7] has pointed out that cooks of aspen made at low concentrations of alkali and with low percentages, followed by chlorination, washing, and bleaching, will give yields of bleached pulp as high as 56 per cent of the wood if a rod mill is available for refining the product, or 53 to 54 per cent if a rod mill is not available. Equally high yields cannot be obtained with very short cooks at high concentrations.

Mitchell, Potter, and Ross[21] studied the effect of concentration of alkali and temperature of cooking on poplar chips and gaged their results by the viscosity of their pulps in cuprammonium solution. They found that pulp with a given lignin content could be made in 4 hours either at low concentration and high temperature or at higher concentration and lower temperature, but to obtain such pulp at maximum yield intermediate concentrations had to be employed, since both high temperatures and concentrations are destructive of cellulose and increase of temperature always lowers the viscosity or "quality" of the pulp.

Aronovsky[1] has made an interesting comparison of a number of cooking chemicals on "residual wood" and on the total organic matter, lignin, pentosans, volatile acids, sugars, and furfural, found in the re-

sidual liquor. When using caustic soda he found no furfural and only traces of sugars. Increasing the time and temperature of the cook or the amount of soda used increased the total organic matter in solution and the volatile acids present as sodium salts. More lignin was present in solution when 40 per cent of soda was used than when 20 per cent was employed, but if the cook was continued for a long time at high temperature the lignin found in solution again decreased slightly. Apparently it is acted on destructively and so no longer reacts as lignin.

The effect of some of the cooking factors on the strength of the fiber when beaten in a pebble mill for different lengths of time is shown in Table 22. The fibers tested were first bleached to a standard color in two stages, the first of which was a chlorination, so results are more comparable with mill operations than if the unbleached fiber had been studied, but it cannot be claimed that the changes shown are wholly due to the cooking conditions. In this table the burst is expressed as points per pound and the tear as the grams per pound per ream on the basis of 16 sheets torn. Both are for a ream of $24 \times 36 = 480$.

TABLE 22

Poplar Cooks at 175° C. for 4.25 Hours

Per Cent NaOH Added	Burst when Beaten, Hours					Tear when Beaten, Hours				
	0	1	2	3	4	0	1	2	3	4
18	20.0	77.0	91.0	107.5	116.5	0.60	1.20	1.25	1.02	0.98
20	16.5	70.0	91.0	97.8	102.4	0.54	1.40	1.31	1.08	1.03
22	16.1	70.4	74.5	85.0	88.3	0.53	1.21	1.08	1.07	0.91
26	13.7	66.4	76.9	83.6	85.8	0.47	0.98	0.81	0.72	0.65

Poplar Cooks for 4.25 Hours with 22 Per Cent NaOH

Temperature of Cook	0	1	2	3	4	0	1	2	3	4
160	15.2	80.8	107.2	117.0	122.0	0.49	1.50	1.51	1.27	1.17
170	19.0	73.6	91.4	103.2	105.6	0.62	1.09	1.23	1.19	1.03
175	16.1	70.4	74.5	85.0	88.3	0.53	1.21	1.08	1.07	0.91
180	18.7	55.7	74.0	77.6	75.0	0.60	0.88	0.84	0.82	0.66

Poplar Cooks with 22 Per Cent NaOH and at 175° C.

Hours at Pressure	0	1	2	3	4	0	1	2	3	4
3	19.0	66.3	89.6	95.5	102.1	0.53	1.25	1.30	1.12	1.07
4¼	16.1	70.4	74.5	85.0	88.3	0.53	1.21	1.08	1.07	0.91
5½	19.8	63.5	84.0	92.0	96.8	0.55	1.23	1.11	0.93	0.87

TABLE 22 (*Continued*)

Maple Cooks at 175° C. for 6 Hours

Per Cent NaOH Added	0	1	2	3	4	0	1	2	3	4
18	15.3	78.9	97.6	110.0	109.0	0.25	0.99	1.03	0.92	0.86
20	18.0	72.6	88.4	95.0	95.6	0.32	0.87	0.80	0.70	0.64
22	17.1	67.3	84.6	88.6	85.5	0.27	0.82	0.72	0.71	0.64
26	20.7	66.0	67.5	58.7	46.7	0.43	0.68	0.62	0.49	0.35

Maple Cooks with 22 Per Cent NaOH and at 175° C.

Hours at Pressure	0	1	2	3	4	0	1	2	3	4
4½	14.9	66.0	83.0	90.4	91.3	0.31	0.84	0.89	0.81	0.73
6	17.1	67.3	84.6	88.6	85.5	0.27	0.82	0.72	0.71	0.64
7½	16.2	65.0	76.0	80.0	72.5	0.33	0.83	0.77	0.73	0.57

Beech Cooks at 175° C. for 6 Hours

Per Cent NaOH Added	0	1	2	3	4	0	1	2	3	4
18	12.2	59.7	80.3	91.5	94.2	0.39	1.06	1.02	0.95	0.86
20	12.1	62.7	79.0	86.2	87.5	0.42	0.98	0.95	0.92	0.79
22	11.4	62.6	75.6	81.6	73.0	0.39	0.93	0.90	0.83	0.64
26	14.5	60.1	69.4	65.0	46.5	0.46	0.76	0.66	0.61	0.43

Beech Cooks with 22 Per Cent NaOH and at 175° C.

Hours at Pressure	Burst when Beaten, Hours					Tear when Beaten, Hours				
	0	1	2	3	4	0	1	2	3	4
4½	11.5	61.3	77.2	82.6	77.7	0.41	0.99	0.91	0.83	0.72
6	11.4	62.6	75.6	81.6	73.0	0.39	0.93	0.90	0.83	0.64
7½	12.4	54.7	70.0	71.0	66.2	0.41	0.74	0.72	0.59	0.47

Yellow Birch Cooks at 177° C. for 6 Hours

Per Cent NaOH Added	0	1	2	3	4	0	1	2	3	4
18	14.8	86.0	108.8	125.0	126.0	0.65	1.74	1.52	1.30	1.14
20	16.2	71.0	100.5	105.0	117.7	0.71	1.68	1.30	1.25	0.99
22	15.5	77.0	97.5	99.7	102.8	0.70	1.55	1.27	1.16	0.96
26	17.4	70.1	84.3	85.3	82.8	0.89	1.31	1.01	0.89	0.76

Yellow Birch Cooks with 22 Per Cent NaOH and at 175° C.

Hours at Pressure	0	1	2	3	4	0	1	2	3	4
4½	15.3	72.5	97.5	107.0	113.0	0.69	2.00	1.70	1.29	1.12
6	15.5	77.0	97.5	99.7	102.8	0.70	1.55	1.27	1.16	0.96
7½	18.6	73.1	88.5	95.6	96.5	0.99	1.47	1.21	0.96	0.85

TABLE 22 — *(Concluded)*

White Birch Cooks at 175° C. for 6 Hours

Per Cent NaOH Added	0	1	2	3	4	0	1	2	3	4
18	20.5	87.8	101.4	115.5	123.0	0.76	1.52	1.43	1.38	1.19
20	18.7	79.4	99.1	99.7	104.0	0.69	1.41	1.19	1.10	1.00
22	18.6	79.0	87.7	89.2	92.8	0.70	1,36	1.06	0.96	1.85
26	24.9	76.8	80.0	80.5	69.8	1.04	1.08	0.81	0.67	0.59

White Birch Cooks with 22 Per Cent NaOH and at 175° C.

Hours at Pressure	0	1	2	3	4	0	1	2	3	4
4½	18.6	77.4	91.4	101.2	105.5	0.77	1.67	1.31	1.18	1.01
6	18.6	79.0	87.7	89.2	92.8	0.70	1.36	1.06	0.96	0.85
7½	20.3	78.9	96.5	97.2	91.5	0.75	1.35	1.09	0.99	0.84

From these and other investigations (including tests for fold, shrinkage, and slowness) it appears that the more severely the fiber is cooked the more rapidly the maximum tear is reached and the lower is its value. Severe cooking also decreases the bursting strength for a given time of beating, but increases shrinkage and slowness. The time at full temperature has much less influence on the strength of the fiber than either the temperature of cooking or the amount of caustic soda added.

Comparison of the different woods shows that maple is inferior to poplar in nearly all characteristics, especially tear and shrinkage. Beech is the poorest of all for burst and fold, and except for maple is the poorest for tear. White birch is appreciably better than poplar in several respects, especially tear and fold, while yellow birch is superior to all the others and gives exceptionally high bursting, tearing, and folding tests.

The moisture content of the wood is of importance chiefly in connection with the necessary adjustment of the strength of the cooking liquor. If the final concentration of the caustic soda, taking into account the water in the wood as well as that in the liquor itself, is kept constant, the same yield will be obtained, whether the chips contain 5 or 22 per cent of moisture. It is believed in some quarters that even though the yield may remain the same the fiber produced from very wet wood (50 per cent moisture) has better strength than that from wood with half as much moisture.

The causticity of the cooking liquor has practically no influence on the cooking process provided the correct amount of actual caustic soda is present. This is easily assured by making the proper chemical tests,

but if reliance is placed on hydrometer tests it is quite possible that in-sufficient caustic may be present. It is true, of course, that the caus-ticity of the cooking liquor has a considerable effect upon the economy of the cooking and recovery processes, since the carbonate is carried through the system as so much inert material which must be handled by the evaporators and black-ash burners and is subjected to a loss of 10 to 20 per cent during each cycle. It has been estimated that, in a plant making 70 tons of fiber per day, each increase of 1 per cent in causticity means an annual saving of about $500.

In diluting the liquor to the proper strength for use it is the custom of some mills to add a certain proportion of black liquor. This is done with the idea of more completely utilizing the alkali in the black liquor and obtaining a more concentrated liquor to go to the recovery system. As it is in direct line with the production of brown " kraft " fiber it is logical to expect that the bleaching properties of the fiber would suffer, and this was found to be true in laboratory cooks when black liquor of relatively high concentration was used. If 8 per cent of the total liquor was black liquor the bleach required was increased from 8.4 to 10.1 per cent, while 17 per cent of black liquor raised it to 14.1 per cent. If no fresh liquor was used, but the entire charge was made up of black liquor brought to the correct strength by adding caustic soda, the fiber produced required at least 22 per cent of bleach. In contrast to this it has been found in mill operations that as much as 25 per cent of weak black liquor can be added to the charge without any appreciable increase in bleach requirements. There is some evidence that the yield of fiber is slightly increased and its strength a little better than that cooked without black liquor.

Any consideration of the time of cooking at once brings up the question of the speed of the reaction between wood and caustic soda. Fortunately this can be followed very readily by means of analyses of the cooking liquor used and of the black liquor at different time inter-vals. From these data the consumption of caustic soda may be calculated by the following formula:

$$X = C - \frac{B \times C}{A}$$

where X = per cent NaOH used up, based on the bone-dry wood,
A = per cent causticity at the start,
B = per cent causticity at time of sampling black liquor,
C = per cent NaOH added on bone-dry wood.

Figure 23 shows graphically the results of three such studies on poplar wood. Curve A was obtained from a vertical stationary digester hold-

ing 400 pounds of wood; B is from a rotary digester holding about 3 cords; while C is from a vertical stationary digester of a capacity of 14.5 cords of wood. All three cooks were made at 110 pounds of steam pressure, and the ratio of wood to alkali was the same for all. In each study the percentage of caustic soda consumed was based on the bone-dry wood. The weight of wood used in the largest digester was
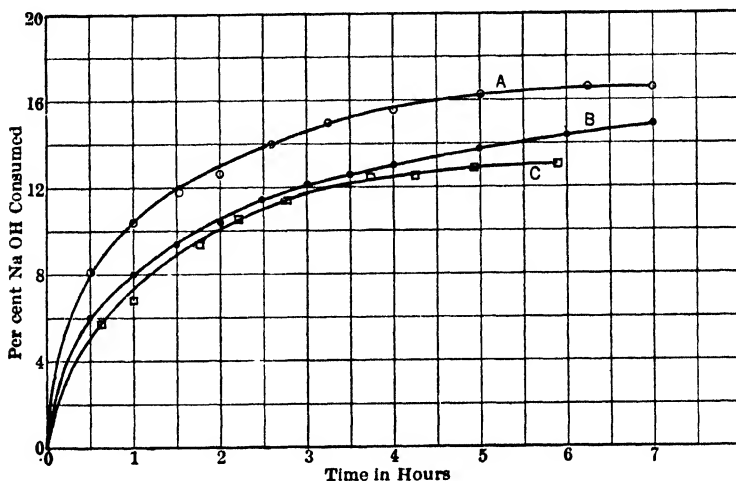

FIG. 23.   RATE OF CAUSTIC CONSUMPTION.

estimated from the average weight of a cord of poplar, but in the other two cooks the chips were accurately weighed; this may have introduced a slight error into curve C, but this would merely alter its position on the chart and would not change its form.

These curves are characteristic of the soda process. The difference between small and large cooks is probably due to the differences in the speed with which they heat up, and in fact by forcing the steaming in the rotary digester it was possible to make the curve almost exactly duplicate curve A, both in form and position. They also explain why the time factor is of minor importance, for the reaction is one of such great rapidity that over half of the total alkali consumed in a 7-hour cook is used up during the first hour, in spite of the fact that during most of this time the charge is being brought up to pressure.

From a series of cooks on aspen, loblolly pine, and jack pine, Wells, Grabow, Staidl, and Bray[34] found that about 90 per cent of the cooking occurred in the first 2 hours. Those constituents of the wood which form acetic, formic, and other volatile acids are very easily hydrolyzed,

and the greater portion is removed even before the digester has reached pressure. At the beginning of the cook the cellulose is removed as fast as the lignin, and it is only in the middle portion of the cook that the lignin removal is more rapid than that of the cellulose. With jack pine the methoxyl found in the pulp decreases rapidly for the first 2 hours and then falls slowly. They also found that the point of maximum bleachability could be passed and that further cooking seemed to dye the fiber and increase its bleach requirement.

Tests on Engelmann spruce and red alder have given results which practically duplicate the curves of Fig. 23, while Heuser[14] obtained very similar results with beech wood. Christiansen,[6] on the other hand, claims to have established the fact that there are points at which the reaction ceases for a while and then begins again. These pauses are of different duration and take place at different periods during the cook. Some cooks show two such pauses, some one, and some not any, and a careful study of his work leads to the belief that they are probably due to the methods of sampling and analyzing the black liquor. A careful scrutiny of poplar cooks has failed to show any trace of such a pause which was not readily explained by the difficulty in obtaining a representative sample of the black liquor in the digester.

From the speed with which the cooking takes place it would seem that penetration of the chips by the caustic soda must be very rapid and that little would be gained by the use of wetting agents, such as the sulfuric esters of the higher alcohols, the sulfonates of substituted naphthalene, etc.[32] Laboratory tests of three such agents have shown no significant change in yields for either poplar or yellow birch, while the strength of the fiber from poplar was slightly higher for burst and tear but unchanged for fold. Yellow-birch fiber had the same strength, either with or without the wetting agent.

The methods of analysis used in determining the rate of reaction make possible also a study of the relationship between the caustic consumed and the yield of fiber obtained. The results of such an investigation were published in 1912,[29] and from this paper the curves for spruce and poplar in Fig. 24 are reproduced. This work indicated that up to the point where the consumption of caustic soda amounted to 14 per cent, based on the dry wood, there was merely a softening of the chips and almost no separation into fibers. Between 14 and 19.5 per cent consumption seemed to be the critical stage in which the transition from chips, through shives to commercially satisfactory fiber, took place. Beyond 19 per cent consumption the decrease in yield bore a constant ratio to the increase in caustic consumption and the reaction appeared to be largely a destruction of the cellulose. The results from

cooks of spruce chips gave a very similar curve, but the yield for a given consumption of caustic soda was considerably lower than for poplar.

These conclusions were based on cooks made in part in the gas-heated digester, and recent cooks under less severe conditions indicate that the caustic consumption for a given yield is less than is shown by the curve for poplar in Fig. 24. The available data from the latter series
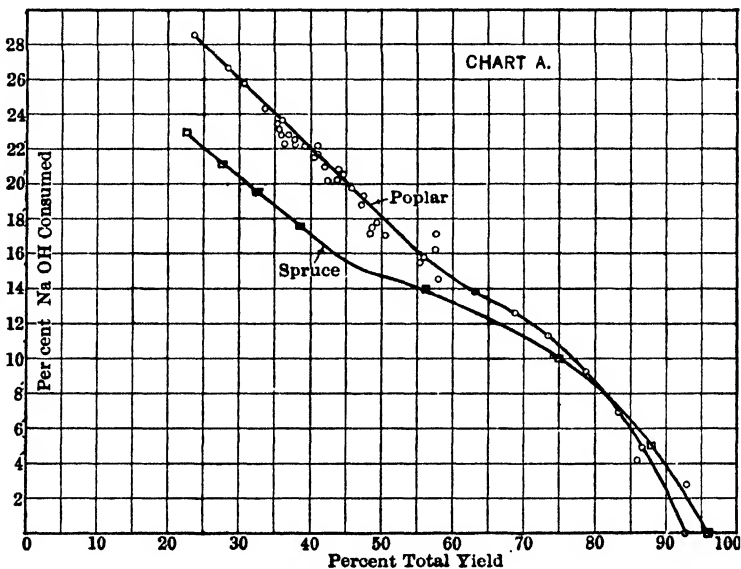

FIG. 24.   YIELD *vs.* CAUSTIC CONSUMED.

do not cover a wide enough range of conditions to allow a good comparison to be made, but it appears that the curve would be shifted to the left in the chart but remain approximately parallel to the former curve.

The amount of fresh soda ash which it is necessary to add per cord of wood cooked varies with the percentage of soda which is recovered, as is shown in the following tabulation of data from a number of soda mill records:

KIND OF WOOD COOKED	RECOVERY Per cent	SODA ASH PER CORD Pounds
Poplar	87.5	153
Poplar	76.0	184
Poplar and hardwoods (about equal weights)	86.3	163
Poplar and hardwoods	{ 83.9	189
	{ 78.3	220
Poplar (40%), gum (60%)	85.7	157

It is customary to figure that the soda ash necessary to make up for losses will be about 300 to 500 pounds per ton of pulp, and to provide 500 to 550 pounds of quicklime for recausticizing the recovered ash.

The present tendency in soda cooks is toward shorter times than formerly. The success of these shorter cooks depends very largely on vigorous circulation and a rapid supply of steam, and where these conditions are met there is no obvious reason why deciduous woods should be cooked longer than 4 hours or coniferous woods longer than 6. It is claimed that by removing the air from the chips and using superheated steam quicker penetration of the liquor may be obtained and the cook hastened. In view of the extremely rapid penetration of the liquor under normal conditions it is very doubtful if any appreciable decrease in the cooking time can be obtained in this way.

There have been proposals at various times to modify the regular soda process by the addition of small amounts of other chemicals, such as salt or sodium nitrate, the idea being that they exert a protective action and thus give better fiber or more of it. So far as is known none of these modifications has ever been used in more than an experimental way. Another modification was that of Freeman,[11] who proposed to carry out the cook in an atmosphere of hydrogen. Still another proposition was to saturate the chips with cooking liquor, draw off the excess, and complete the cook by steaming as usual. This is directly opposed to the present thought that enough liquor should be present at the start of the cook to cover the chips completely.

The use of small quantities of sulfur in the cooking liquor is a modification which has received much attention. It was first claimed that the use of about 0.2 per cent on the weight of the wood would materially increase the yield without causing a serious nuisance by its odor. Attempts to confirm this claim showed that under a given set of cooking conditions the woods respond differently, as is seen from the following table:

KIND OF WOOD	PERCENTAGE YIELD ON BONE-DRY BASIS	
	Without sulfur	With 0.2 per cent of sulfur
Poplar	38.9	41.9
Spruce	36.8	35.7
White birch	40.9	40.9
White maple	40.6	41.4
Yellow poplar	41.7	42.6

In all these trials the fiber produced with sulfur bleached more easily than the other. This was also found true by Spence,[26] who used about 1.1 pounds of sulfur per 100 pounds of fiber produced and saved about

5 per cent of the normal bleach requirement. Under his conditions of operation it required 1.1 pounds of sulfur to save about 0.92 pound of 35 per cent bleach.

Somewhat larger additions were studied by Wells,[33] who added 2 pounds of ground sulfur to a digester containing 100 pounds of jack-pine chips and 20 pounds of caustic soda. He found that sulfur speeded up the reaction and gave pulp with greater tearing, folding, bursting, and tensile strength. It appeared that the fiber from sulfur-containing cooks was tougher and required longer treatment to develop its maximum strength. If the cooks were made under conditions to give equal yields the pulp from those with sulfur required only about half as much bleach as the others. It seems to be generally accepted that small amounts of sulfur are more beneficial for coniferous woods than for poplar and hardwoods.

Bray, Martin, and Carpenter,[4] when cooking white pine by the soda process, found that the addition of 2 to 4 per cent of sulfur on the weight of the wood was beneficial to the strength and bleaching qualities of the fiber, but that it had very little effect on the yield. The sulfur seemed to render the dyes and ligneous substances more active toward caustic soda, or to produce more soluble compounds which were less likely to reprecipitate on the fibers.

Burton[5] combined a mechanical treatment with the soda process by cooking in drums furnished inside with loose rollers of steel, or of steel filled with lead, while Muntzing[22] placed the logs in the digester without chipping and as the fibers were rubbed off they were quickly removed from the sphere of action by pumping the liquor through a filter press. The clear liquor was returned to the digester. So far as is known neither of these processes has found any practical application.

The blow-off from the digesters when cooking pines contains considerable turpentine and its recovery is mentioned in Chapter IV. Besides turpentine there are other materials of an easily volatile nature. From the relief of a poplar cook, a small amount of an oil and a liquid containing aldehydes, ketones, alcohol, acetone, etc., have been condensed. From small-scale cooks Bergström[2] has found the yields of alcohol based on the dry wood to be 0.66 to 0.68 per cent for *Picea excelsa, Pinus silvestris, Pinus palustris, Pinus echinata,* and *Populus tremuloides,* and 0.81 to 0.83 per cent for *Betula alba* and *Eucalyptus.*

The composition of three samples of the material blown from the digester, taken during the entire time of discharge, was found to be as follows:

	SAMPLE 1 Per cent	SAMPLE 2 Per cent	SAMPLE 3 Per cent
Fiber (bone dry)	11.38	8.15	7.32
Alkali as Na_2O	4.14	4.06	2.92
Organic matter and CO_2	10.76	11.31	8.24
Water	73.72	76.48	81.51

The washing of soda fiber is usually carried out in open tanks, rather than in the diffusers of the sulfate process, but in some cases rotary filters are used. Wash pits are merely iron tanks with perforated false bottoms, which retain the fiber and allow the liquor to pass through. They are usually of such a size as to contain the entire charge of a digester and allow room above the stock for flooding with water. Pits of this sort for a 15-cord digester would be about 19.5 feet in diameter by 13 feet deep above the false bottom, which has a 2-inch pitch toward the central outlet to aid in washing out the stock. One digester charge fills one of these pits to a depth of about 7.5 to 9.25 feet when leveled off, which corresponds to about 66 to 82 per cent of the digester capacity.

The charge is washed first by flooding with weak liquor from a previous wash; the liquor taken off during this period goes to the recovery plant. The next wash is with hot water, which produces the weak liquor used in the first flooding of a subsequent cook, and the final washing is with hot water, which runs to waste as it is too weak to pay for evaporation.

In some mills the weak liquor is collected in tanks before being pumped onto the next pit, but in others it is pumped directly from one wash pit to the next. This latter, or " cycle system," requires less space and produces stronger liquor, but it requires more time to complete a wash, and it is often necessary to hold a pit of stock with the black liquor on it, which injures its bleaching properties. Spence[27] states that with hardwood cooks the liquor from the digester tests 12° Bé. at 60° F., while that going to the evaporators tests 9°. With the cycle system the latter would test $10\frac{1}{4}$° Bé. instead of 9°, which would mean a saving in evaporation of 46,000 gallons per day for a plant with a daily capacity of 100 tons of pulp.

The washing time depends largely on the depth of stock which the wash water has to penetrate, the temperature of the wash water, the kind of wood, and the nature of the cook. The greater the drainage area per ton of fiber the more rapid will be the washing, but if the depth of stock is too small the recovery is not so great and the liquor is weaker. Beveridge[3] mentions installations where the area per ton was as low as $7\frac{1}{2}$ square feet, but considers this far too little, and recom-

mends 35 square feet for poplar and 45–50 for chestnut. Hardwood fiber drains slower than northern poplar, and overcooking slows down drainage.

With poplar fiber the approximate washing data for the 19½-foot tanks mentioned above are as follows:

	First Wash	Second Wash	Third Wash
Time of washing, hours..	4–7	5–8	2–3
Volume of liquor taken off, gallons	18,000 —19,000	19,000 —20,000	..
Baumé at end	5° at 70° C.	0° at 50° C.	..

Under these conditions the recovery of the soda entering the pit is about 98.5 per cent and the strong black liquor obtained contains about 0.63 to 0.65 pounds of soda per gallon.

The use of hot water greatly increases the speed of washing, but cold water, if given enough time, will remove impurities just as completely. If the fiber stands for any appreciable time in contact with the black liquor it seems to absorb coloring matters and becomes very hard to bleach. This is not so serious if the charge remains hot, but if it becomes cold the bleach required may be very greatly increased, sometimes by as much as 5–6 per cent on the weight of fiber. On general principles, then, the stock should be washed as soon as possible after blowing from the digester, and access of air and cooling should be minimized. It is particularly important that the last traces of black liquor be removed in order to save bleach and obtain whiter fiber.

There is always a slight loss of fiber during the washing out of the black liquor, but much of this can be recovered by screening the liquor before it goes to the evaporators. The amount of this loss through the wash-pit bottoms will range from 0.2 per cent up to 1.0 per cent of the fiber handled, according to the condition of the pit bottoms and the care used by the men. Spence[28] gives it as 700 to 1200 pounds of fiber per 350,000 gallons of liquor drawn off. Other fiber losses occur regularly in all operations where the fiber is washed, or concentrated by removal of water. These losses depend so much on local conditions and equipment that no figures of any value can be given.

In some mills the washing of the black stock is now performed on continuous filters, the stock after blowing being diluted with strong black liquor until it is of such a consistency that it can be pumped to the filter. It is claimed that there is less loss of fiber and that washing is more complete with less wash water, thus producing a black liquor of higher concentration to send to the evaporators. As compared with the usual wash-pan system the claims are as follows:

	FILTERS	PAN SYSTEM
Pounds wash water per pound dry fiber	5–7	16–20
Baumé of liquor to evaporators	11	6–9
Soda in washed fiber, per cent	0.2–0.8	1.4–1.6

After washing the treatment of the pulp is largely mechanical until it reaches the bleaching system. It is sluiced out of the wash pits by a heavy stream of water and run through screens to remove shives, uncooked pieces, or knots. It goes next, while in a highly diluted condition, over sand settlers which are long, shallow troughs with crossbars at intervals in the bottom, and in which sand, dirt, cinders, shives, and other impurities settle out. From the sand settlers it goes to a series of extractors which remove a large part of the water and deliver the pulp at a proper concentration for bleaching. During these processes the amount of water present per pound of bone-dry fiber has been found to be about as follows:

	POUNDS
In wash pits	9–11.5
At knotters	87.7
At centrifugal screens and sand settlers	123–135
Entering bleaching system	24.5–27
Entering high-density bleachers	4.5–7.5

Soda pulp from poplar and hardwoods will bleach to a good white color with 8 to 12 per cent of bleaching powder, while that from coniferous woods requires considerably more. Modern methods of bleaching have enabled much whiter fiber to be obtained without appreciable loss in strength.

Black Liquor. The black liquor removed from the fiber during washing contains nearly all the alkali originally employed, together with the organic matter from about half the weight of the wood. Griffin[12] claims that the liquor in the digester is light rose in color, but that it immediately darkens on exposure to air.

An analysis of black liquor from poplar showed that the total alkali, equivalent to about 65.5 grams per liter of sodium carbonate, was combined as follows:

> 25.8 per cent as acetate.
> 8.0 per cent as carbonate.
> 13.3 per cent as hydroxide.
> 13.5 per cent with insoluble organic acids.
> 39.4 per cent with soluble organic acids.

This proportion of soda as hydroxide is much less than that necessary according to Klason,[17] who believed that 40 per cent of the total alkali must remain unused in the black liquor and that even if the wood were

present in great excess at least 25 per cent of the alkali would be un-consumed. It has not proved possible to confirm Klason's statement when cooking poplar wood. If less than 9 per cent of NaOH is added, the wood uses it up completely, and even when 18 per cent on the weight of wood is added, fully 90 per cent is consumed and the black liquor contains only 1.4 grams per liter. The analyses in Table 23 of black liquors from cooks of different woods on a semi-commercial scale also show much less caustic remaining than Klason's theory calls for.

TABLE 23

Kind of Wood	Black Liquor		Caustic Remaining. Per Cent on Bone-Dry Wood
	Grams per Liter NaOH	Per Cent Causticity	
White maple.......	13.1–14.3	21.1–21.4	5.0– 5.1
White birch........	8.7–21.5	12.2–28.8	2.9– 7.7
Black gum.........	20.2–22.1	33.3–35.6	9.8–10.4
Beech.............	10.6–17.6	18.5–21.3	4.6– 4.8
Poplar............	6.4–18.1	15.3–29.1	3.5– 8.0

Among the chemicals which have been recognized in black liquor are the sodium salts of formic, acetic, and oxalic acids, and a number of patents have been taken out for their recovery.[16,9] Humic matter precipitated from the liquor by carbon dioxide or acids has been pro-posed as a paper size, or as the base for sulfur dyes or nitrated coloring matters, but apparently none of these proposals has ever developed commercially. Destructive distillation in such a way that the gases and volatile oils could be collected and used while the alkali remained in the residue was advocated at one time, and it was hoped to obtain methyl alcohol, acetone, aldehydes, amines, phenolic oils, etc. It was found that under normal business conditions these products could be obtained more cheaply from other sources. Such a distillation method on black liquor from the straight soda process was reported to have given the following materials per ton of pulp:[15]

	KILOGRAMS
Methanol	10
Acetone	8
Butanone	10
Higher ketones	6
Light oil	4
Heavy oil	52

A Swedish mill, using the same process, obtained about twice these yields.

More recently[23] precipitation of organic matter from the black liquor by carbon dioxide has been taken up again, and it is said that about 30 per cent of the total organic matter is obtainable. When washed and dried, this material is insoluble in water but soluble in dilute alkalies and in most of the polar organic solvents. It has a melting point of about 200° C. in the oven-dry condition, or about 100° C. if it contains 10 per cent of water. It has possibilities in a number of fields, as water treatment, ceramics, and plastics.

Recovery of Soda. The regeneration of the soda in the black liquor is necessary both for reasons of economy and because of the difficulty of disposing of such large quantities of waste liquor in any other way. Fortunately the liquor is of such a nature as to make recovery especially easy from a chemical standpoint, for it contains about one-half of the fuel value of the wood in such a form that its combustion furnishes most of the heat necessary to evaporate the liquor to the point where it can be ignited. In modern installations, where complete combustion of the organic matter takes place, a very considerable amount of excess steam is also produced.

The liquor obtained from the wash pits must be concentrated to at least 30° Bé. at 130° F., or better to 40° Bé. or higher, before it will maintain continuous combustion. This entails the evaporation of a large amount of water and explains why dilution of the liquor during cooking, washing, etc., should be avoided as much as possible.

The proportions of organic and inorganic constituents in a black liquor which tested 12¾° Bé. at 70° F. are approximately as follows:

	GRAMS PER LITER	PER CENT BY WEIGHT	PER CENT ON TOTAL SOLIDS
Total solids	180.2	16.4	....
Water	917.3	83.6	....
Caustic soda	19.5	1.8	10.8
Total alkali as Na₂O	49.9	4.5	27.7
Organic matter precipitated by H₂SO₄	27.3	2.6	15.2

In modern installations the evaporation of soda-process black liquor is carried out in the same types of equipment used for sulfate liquors.

The data of Table 24 show the effect of pressure on the boiling point of black liquor from poplar cooks by the soda process.

The evaporated black liquor which goes to the old type of black-ash furnace contains about 60 per cent solids and enters at about 200° F. Unlike the sulfate process, smelters do not generally accompany this

type of furnace for soda black liquor and the burning is carried to a point where the ash can be leached for recovery of soda.   If the furnace is working properly the ash discharged is in a glowing condition and shows at most only a slight blue flame, but if it is underburned because of an overloaded condition of the furnace it may show considerable yellow flame, even after it is dumped into the leach tanks.   Under ordinary conditions a 20-foot furnace, operated by experienced men, will produce 30 to 33 tons, or even more, of ash per day, containing 65 to 80 per cent of sodium carbonate, according to the care with which it is burned.   The balance of the ash is largely carbon, with small amounts of iron, alumina, lime, sulfur, and silica derived from various sources.

TABLE 24

Degrees Bé. at Room Temperature	Grams Dry Matter per 100 Grams Liquor	Boiling Points in Degrees C. at *				
		41 Inches Pressure	20 Inches Pressure	0 Inches Pressure	10 Inches Vacuum	25 Inches Vacuum
7	7.8	124.5	114.3	101	90.5	58.5
16	18.5	.....	.....	...	.....	....
22	27.1	128.0	117.5	104	93.0	62.0
27	36.6	.....	.....	...	.....	....
32	46.8	.....	.....	...	.....	....
37	57.6	135.5	124.7	112	100.9	69.0

* Records for pressure and vacuum are in inches of mercury.

The fuel used in the fire box of a black-ash furnace may be coal, wood waste, gas, or oil according to location and cost.   The amount of such fuel per ton of ash is usually not recorded carefully because of the general use of waste materials.   During one test of a 20-foot furnace taking liquor at 38 Bé., the coal burned per ton of ash produced was 117 pounds at 2.3 per cent moisture while under similar conditions 325 pounds of shavings with a moisture content of 39 per cent were required.

From this type of furnace the ash goes to some form of leaching device, either open tanks, or closed tanks to which pressure can be applied.   The ash is first flooded with water from below in order to avoid explosions when water comes in contact with the glowing mass. The washing is carried out systematically in order to produce leach liquor of good strength with as little loss of soda as possible.   There seems to be little to choose between the open and closed tanks so far as operating efficiency is concerned.

The material remaining in the leaching tanks after washing is completed consists of a light, porous carbon containing a little soda and small amounts of impurities. The following analysis gives an idea of the composition of the black-ash waste after thorough drying and exposure to air:

	PER CENT
Moisture, H_2O	6.06
Sodium carbonate, Na_2CO_3	2.51
Calcium carbonate, $CaCO_3$	1.17
Sodium sulfide, Na_2S	0.37
Magnesia, MgO	0.34
Iron and alumina, Fe_2O_3 and Al_2O_3	0.26
Silica, SiO_2	0.17
Calcium sulfate, $CaSO_4$	0.07
Carbon by difference, C	89.05

Because of its physical condition black-ash waste cannot be readily separated from its accompanying water by mechanical means. When drained as much as possible in the leach tanks it still contains 80 to 85 per cent of water, and this cannot be reduced below 65 to 68 per cent by centrifugal action. Thoroughly dry waste weighs about 6.9 pounds per cubic foot when tamped into the container.

Attempts have been made to use black-ash waste in making decolorizing carbon, as a paint pigment, in rubber manufacture, and in carbon electrodes, but the amounts so used are small in comparison to that produced. The most promising use is as a fuel, since the heating value of the dried waste is 14,000 to 14,500 B.t.u.

The black-ash-waste problem is entirely avoided in the newer recovery furnaces which burn out the carbon entirely and deliver the soda in the molten condition to the dissolving tanks. The Wagner furnace, which is of this type, is described briefly in Chapter IV, and an account of its operation on soda liquor is given by Millidge, Taylor, and Heimrod.[20] The black liquor normally supplied tests about 35° Bé. at 60° F., but is sprayed into the furnace at about 150° F. and at a pressure of 20 pounds per square inch with air at the spray nozzle at 10 pounds. Complete combustion is obtained in the crucible of the furnace by means of air blasts, and the heat of combustion is such that the gas temperature in the upper part of the furnace is about 1700° F., which is reduced to 450° on leaving the waste-heat boiler and to 170° at the exit from the scrubber.

The scrubber treats the hot gases with water to condition them for soda recovery, and it has been found that this scrubbing removes only about 10 per cent of the total in the gases, or about 528 out of 5300

pounds. From the scrubber the gases go to the Cottrell precipitator which removes 90 per cent of the soda entering it. The soda treated in the fume recovery system is about 7 per cent of the total furnace charge, with an average loss to the atmosphere of 480 pounds of Na_2CO_3, or $8\frac{3}{4}$ pounds per ton of pulp made. The overall soda recovery on a monthly basis is 93 per cent, while the lime recovery in an oil-fired kiln is 85 per cent.

The Tomlinson furnace has recently been tried in the soda process with satisfactory results, but its operation differs somewhat from that in the sulfate process. Liquor of 46 per cent solids from poplar has been found to burn well, but 60 per cent or higher is preferred. It is best to spray it in at the top instead of from the front of the furnace, and it is important to keep the temperature of the liquor up to at least 230° F. and maintain a heavy pressure to insure thorough atomization. One furnace of this type is handling the black liquor from a little over 100 tons of soda pulp per day and is netting approximately 37,000 pounds of steam per hour with prospects of increasing this somewhat.

Summary of Soda Losses. Loss of soda takes place constantly at a number of points and irregularly at many others, because of accidents, carelessness, etc. Of the regular losses the following are rough estimates of what the minimum and maximum should be on the basis of the present best possible operation, and conditions which are about as poor as could be tolerated.

NATURE OF LOSS	LOSS PER TON FIBER LB. Na_2CO_3	
	Min.	Max.
In dilute black liquor	12	25
Evaporator losses	..	28
In washed fiber	10	36
In black ash waste	6	28
In flue gases	9	36
In lime sludge from causticizing	19	50
	56	203

If it is assumed that 1250 pounds of soda ash is used per ton of pulp made, this minimum loss would indicate a recovery of about 95.5 per cent, a figure which is seldom reached in actual mill practice. The maximum loss shows a recovery of about 84 per cent, which is more nearly correct for the older type of mill.

Lime losses depend on the completeness with which it is utilized during causticizing and on whether recovery by reburning is practiced.

Tests and Analyses for the Soda Process. The tests necessary for the control of the soda process are comparatively simple, and the details

of most of the methods can be found in the common textbooks of analytical procedures. The materials which should be tested are the cooking liquor, black liquor, black ash, black-ash waste, soda ash, lime, lime mud, and fiber.

The cooking liquor may be tested with sufficient accuracy by titrating with acid, using the two indicators phenolphthalein and methyl orange. From the test the grams per liter of caustic soda and the causticity of the liquor may be calculated, and from this the proper volume to add to the digester.

Black liquor may be tested for its approximate content of NaOH by diluting 25 cc. with 400 cc. of water, adding 15 cc. of $BaCl_2$ solution (400 grams per liter), and titrating with standard acid using phenolphthalein as an outside indicator on a white spot plate. The end point is not very sharp, but with a little practice concordant results may be obtained.

The total alkali in black liquor is determined by evaporating a known volume to dryness, igniting carefully to burn off the organic matter, extracting the alkali with hot water, and titrating. Care must be taken to avoid volatilizing soda by heating too long or at too high a temperature. It is best not to attempt to burn off all carbon at the first ignition, but to leach out the soda after complete carbonization has taken place, carefully dry the remaining carbon, and ignite again.

The soda in black ash may be leached out, the residue ignited, and the second leaching combined with the first for titration with acid. Black-ash waste should be ignited to burn off most of the carbon before attempting to dissolve the residual soda; the titration is then made as usual.

Soda ash, as ordinarily purchased, is one of the purest of chemicals, but on storage it may take up moisture and carbon dioxide to some extent, so it is well to test it, at least occasionally. Moisture may be determined by heating a sample for an hour at 150–155° C. and noting the loss in weight. Tests for total alkalinity, caustic soda, and bicarbonate are made by the usual volumetric methods.[30]

A complete chemical analysis of lime will not necessarily show its value as a causticizing agent, but there are a number of tests which give comparative data and enable different shipments to be evaluated. One of these is the determination of the available lime empirically by a modification of the Scaife method.[25]

A simple causticizing test, made under conditions similar to mill operations, will also indicate its value for this work. The first requisite is a representative sample, and this is not by any means easy to obtain from bulk shipments. The sample should be crushed and

quartered down as rapidly as possible and from the final sample a weighed amount boiled for exactly 1 hour with water and a weighed amount of soda ash in excess of the amount which the lime can causticize. The amount of water should be so chosen that the final solution at the end of the boil is about the strength of that used in the mill. After completing the boil the sludge should be settled or filtered off and the strength and causticity of the solution determined as for the cooking liquor. The causticity and the amount of soda ash taken being known, the amount of lime required to causticize 100 pounds of soda ash may be easily calculated.

TABLE 25

Equipment	Probable Life	Cost of Annual Repairs
	Years	Per cent
Conveyor drive and structure...............	15	10
Conveyor chain..........................	6	20
Chippers.................................	10	15
Chip screens — shaker type...............	15	8
Digesters................................	30	2
Blow tanks (separators)....................	20	2
Wash pans...............................	30	3
Stock pumps.............................	15	3
Stock pipe...............................	10	2
Screens — centrifugal.....................	15	5
Bleach tanks — concrete...................	30	1
Agitators in bleach tanks..................	10	5
Drainers — concrete......................	50	1
Wet machines............................	10	5
Causticizing tanks........................	25	5
Sludge pumps............................	10	8
Evaporators..............................	25	5
Rotary furnaces..........................	20	10
Leach tanks..............................	25	2

The lime mud, which is a by-product of the causticizing operation, should be tested to see that it is well washed and does not carry off too much soda. A representative sample of the dried mud should be moistened with strong ammonium carbonate solution, evaporated to dryness, heated over a low flame until no odor of ammonia can be noticed, and then leached repeatedly with hot water to extract all the soluble alkali.

Life of Soda-Mill Equipment. The remarks in Chapter IV regarding the life of mechanical equipment apply with equal force to soda mill machinery. The figures in Table 25 are therefore to be considered as approximate estimates only.

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CHAPTER VI

THE SULFITE PROCESS

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The first patent relating to the use of sulfurous acid in preparing pulp from wood was granted to B. C. Tilghman in 1867.[108] This was followed in 1869 by a supplementary patent covering the treatment of fibrous materials at ordinary pressures, and it is upon these two patents that subsequent modifications of the process are based. The specifications of the original patent show that Tilghman had worked out his process experimentally with great care and thoroughness and that he fully understood its possibilities. In its practical application, however, difficulties of an engineering nature arose which proved too serious for him to overcome.

After his failure the process was taken up by Ekman and Fry in Sweden, by Mitscherlich in Germany, by Francke, Graham, Ritter, Kellner, and numerous other investigators and manufacturers, and the engineering difficulties were gradually overcome so that finally the process was established on a firm footing.

Theory of the Sulfite Process. In the sulfite pulping process the cellulose fibers are liberated from the wood by dissolving the lignin and some of the carbohydrate material. It is generally accepted that the principal constituents of the wood, cellulose, hemicelluloses, and lignin are combined chemically in some manner. The pulping process involves two principal types of reactions, which are probably concurrent: the reaction of the lignin with the bisulfite, and the hydrolytic splitting of the cellulose-lignin complex. The mechanism of the removal of the sulfonated lignin has not yet been satisfactorily explained, perhaps because of incomplete knowledge of the structure of the lignin itself. Hägglund[32] has proposed that the relatively rapid sulfonation reaction is followed by a hydrolysis of the lignin-sulfonic-carbohydrate·complex at a rate regulated by the hydrogen-ion concentration. Calhoun and associates,[16] on the other hand, believe that the sulfonation reaction is the more important factor in the rate of delignification and that this rate is governed by both the hydrogen- and

bisulfite-ion concentrations. Whatever the mechanism, the calcium salt of the sulfonated lignin (in the case of calcium-base liquors) is rendered soluble at the temperatures employed in the pulping process. The easily hydrolyzable hemicelluloses are dissolved at the same time. Fortunately the major portion of the cellulose is comparatively stable under the conditions used, but it is by no means unattacked.

Wood and Its Preparation. An important requisite for wood to be used in the sulfite process is freedom from excessive amounts of resin. It is also important that the resin be evenly distributed, for if it is localized at certain points, the wood at those places will remain hard and will cause shives in the pulp. Resin occurs mainly in the resin ducts and rays rather than in the tracheids or fibers.

The presence of heartwood also constitutes a major difficulty, especially in pulping the pines, owing to the concentration and nature of the resinous material in this portion of the tree. As has been pointed out by Schmidt,[36] various proposals for pulping pine heartwood by removing the resins by solvent extraction or by modifying the cooking liquor have not been economically feasible. Herty[37] has suggested for southern pines the use of young, heart-free wood which is available in large amounts. Such a procedure necessitates careful wood selection, and present indications still point to the continued use of the kraft process for the largest production of southern pine pulps.

The species most commonly used for sulfite pulp are spruce, balsam, hemlock, and the white or true firs. Though most hardwoods are readily reduced, their use has been limited by their short fibers and the relatively low strength of the pulps prepared from them.

In the sulfite process the liquor has less solvent power than the alkali used in the soda process, and any bark, decayed portions, or knots which go into the digester are likely to appear as dirt in the finished pulp. For use as unbleached fiber this applies also to the light-colored inner bark since it changes color and shows as dark fibers in the pulp. For bleached pulp this inner bark is harmless, since it bleaches quite as readily as the rest.

Removal of the bark is accomplished practically in a number of ways. Farmers and settlers often use draw knives. Hand peeling in the woods with a long-handled chisel, or spud, is not so common for spruce though quite general for the poplar used in the soda process. Disk or knife barkers of various types are commonly used in mills where the cleanest possible wood is essential, or to supplement drum barkers. The block of wood is held by hand or machinery against knives fastened to a rapidly revolving disk. These knives remove much wood with the bark, particularly when the sticks are crooked. The amount of such

loss depends on the size of the logs as well as on the care with which the work is done; the sound wood lost may amount to 8 to 20 per cent of the original weight of the logs, in addition to the 8 to 10 per cent of true bark.

The drum barker removes the bark by rubbing the logs against one another and the sides of the drum, and saves most of the loss of wood. It is expensive to install, however; it requires more power than other barkers for the same amount of work, and in winter the water used in it must be heated, which adds to the expense. This type of barker is suitable only where very clean pulp is not essential or where bleached pulp is to be made, as it does not remove all the thin inner bark. It works best on wood which has been in the water two or three months as the bark is then more readily removed. Another type of barking machine is the stationary barker consisting of a series of pockets into which full-length logs lying parallel to each other are fed continuously. Large cams at the bottom of the pockets are slowly rotated to lift the logs and roll them against one another to remove the bark.

For barking large logs, either round or split, or slabs, in mills on the Pacific Coast specially designed machinery is sometimes used in addition to the equipment described above. The methods consist essentially in moving the wood past rotating cutters of various types.

With any system of barking the logs should be inspected on the conveyor as they go to the chipper, and any with bark remaining in cracks or around knots should be put at one side to be cleaned by boring machines or routers, or by hand with an ax. Some operators clean very little by hand but put the defective wood at one side to be cooked separately into second-grade stock. This necessitates a very thorough cleaning up of all apparatus afterwards.

The barked wood next goes to the chippers, which should be run slowly enough to produce even chips. The length of chip depends on the method of cooking as well as the kind of wood. For hemlock they should be $\frac{1}{2}$ to $\frac{3}{4}$ inch long; for spruce they should be about $1\frac{1}{4}$ inches long for Mitscherlich and $\frac{5}{8}$ to $\frac{3}{4}$ inch long for other grades. The coarse chips are generally crushed to reduce their size further and are then screened to remove coarse pieces, which are rechipped, and sawdust, which goes to waste. The sawdust from chipping should not amount to more than 3 per cent.

Uniformity and cleanliness of chips are essential to clean pulp and good yield, and all chips cooked in the same charge should be of one kind of wood and as nearly as possible of the same age and moisture content. In European practice wood grown on different soils, under different climatic conditions, or even on northern and southern slopes,

is not handled in the same way. In American practice the importance of growth and wood variables on the yield and quality of sulfite pulp is gaining recognition.[20]

The moisture content of the chips may vary widely, depending upon the seasoning. Wet chips tend to pack more and cook more slowly than dry chips and may sometimes add to the difficulty in maintaining the acid strength during warm weather. Usually a moisture content of about 30 to 40 per cent is preferred. On the other hand, some woods which cannot be cooked at all if charged dry will cook fairly easily if saturated with water by preliminary boiling and cooling before charging.

Liquor Making. The liquor or acid used in the sulfite process is an aqueous solution of sulfurous acid in which lime, or some other base, has been dissolved; the final result is therefore a solution of the bisulfite of the base containing an excess of sulfurous acid. In practice this is prepared either by passing the gas through water in which the base is dissolved or suspended, or by bringing the gas into contact with comparatively large lumps of the carbonate of the base which are moistened by a continuous flow of water. The first effect of this treatment is the solution of the gas in water forming sulfurous acid:

$$H_2O + SO_2 = H_2SO_3$$
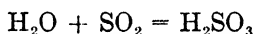
This then attacks the base according to one of the following reactions:

$$Ca(OH)_2 + H_2SO_3 = CaSO_3 + 2H_2O$$

or

$$CaCO_3 + H_2SO_3 = CaSO_3 + H_2O + CO_2$$
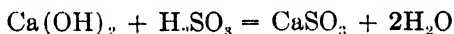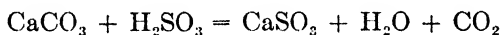
If the base is soda or magnesia the sulfites stay in solution, but if lime is used calcium sulfite is precipitated as fast as it is formed since it is very insoluble, 1 part requiring about 800 parts of cold water for its solution. In the first method, working with milk of lime, the formation of sulfite continues until all the lime is precipitated; further passage of the gas then causes this to redissolve with formation of the bisulfite. When limestone or dolomite is used, as in the second method, its surface gradually crusts over with the sulfite which is again brought into solution as more gas is dissolved. Both these reactions doubtless take place simultaneously when there is a liberal supply of gas.

Preparation of Sulfur Dioxide. Sulfur dioxide for use in the absorption system is prepared by burning either sulfur or iron pyrites; with proper care good results can be obtained by either method. Although the use of sulfur is by far the more common, the choice of the two

processes depends to a great extent on local conditions, such as the relative cost of the two materials, the possibility of disposing of the spent oxide from the pyrites, and the floor space available; it is much more of a financial problem than a technical one.

Sulfur burning was formerly carried on very largely in the retort type of furnaces into which the sulfur was fed through a door at one end. This produced gas of irregular composition owing to the sudden rush of cold air into the furnace and through the apparatus. This type of furnace was suitable for very pure sulfur, but when there was a tendency for the sulfur to form an oily surface scum during burning good results were not obtained. This trouble can be overcome by installing rakes which travel slowly back and forth, breaking up the scum and presenting fresh surfaces for combustion. With this device the flat burners give excellent results.
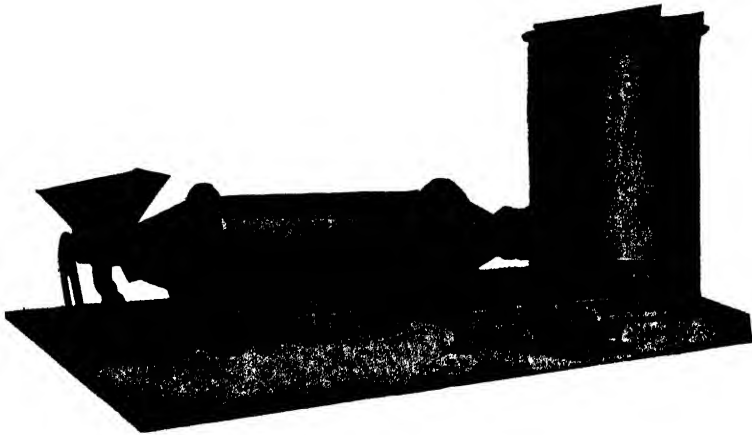
FIG. 25. ROTARY SULFUR BURNER.

Modern sulfur burners are of two types. The rotary burner, illustrated in Fig. 25, is most common. The sulfur enters from the hopper at the front end and gradually works toward the back. As the burner revolves, the sulfur is carried up the sides and thus presents a large and continually renewed surface for combustion. A highly successful modification of the sulfur feed is to introduce it in the molten condition through a pipe entering at the axis of the burner. A continuous supply of molten sulfur may be obtained by placing the crude sulfur in a steam-jacketed tank and also surrounding the delivery pipe with a steam jacket so that the sulfur will not solidify before it reaches the burner. Users of this type of burner claim that it is the best if it is fitted with a self-feeding device and a large combustion chamber be-

cause it makes stronger and more uniform gas and starts and stops very quickly in the event of shutdowns.

The spray-type burner is a recent development[57] in the burning of sulfur. Molten sulfur is pumped through a spray nozzle into one end of a horizontal brick-lined combustion chamber. A water-tube waste-heat boiler has been used in connection with the spray-type burner to utilize some of the heat for generating steam and to cool the gases partially. The principal advantages claimed for the spray-type burner are the possibility of quicker starting and stopping, the formation of smaller amounts of SO_3, and, with proper regulation of the air supply, the formation of higher percentages of SO_2 than are obtained with other types.

The most important factor in sulfur burning is the regulation of the air supply. One pound of sulfur requires for its complete combustion just 1 pound of oxygen, which is the amount contained in 53.8 cubic feet of air. If much more air is admitted, and particularly if it contains much moisture, there is formation of SO_3 and sulfuric acid which causes loss of both lime and sulfur. According to Frohberg,[28] the maximum formation of SO_3 takes place at 400° to 500° C., while at 900° to 1000° C. it is again broken up into sulfur dioxide and oxygen. He recommends running the furnaces as hot as possible to produce rich gas which should then be at once sprayed with cold water to reduce its temperature to 90° to 100° C. In modern mills the temperature of the gas leaving the combustion chamber generally runs from 700° to 1000° C.

According to Cosler,[19] poor cooling may be responsible for excessive formation of SO_3, weak cooking acid, and low free SO_2. Acid saturated with $CaSO_4$ may carry into the digesters as much as 55 pounds per ton of chips. This is largely precipitated at the temperature of cooking and may cause poor penetration and necessitate a high temperature to finish the cook. Methods for eliminating or reducing the SO_3 in the gas are afforded by the Cottrell electrical precipitation process or by filtering the gas through sawdust, although neither is generally used.

Any overheating of the burner is likely to cause vaporization of unconsumed sulfur which passes along with the gases until it reaches the colder portions of the system, where it condenses. Sublimation of sulfur also occurs when too little air is admitted after the burner has become thoroughly heated up since then too little oxygen is present to combine with all the sulfur vapor. The sublimation of sulfur is likely to lead to the formation of thiosulfuric and polythionic acids, which at the temperature of cooking again break down with the liberation of sulfur. Free sulfur may also appear in the acid from direct contami-

nation with sublimed sulfur. Klason claims that the presence of 250 mg. per liter of flowers of sulfur in a liquor would ordinarily convert all the calcium into calcium sulfate. However, under normal conditions the fresh liquor contains only about 3 mg. per liter of sulfur, and the danger from this source is not great.

The conditions under which a burner is working may be judged from the appearance of the flame. When operating satisfactorily it is blue, sometimes tipped with white; brown fumes of unconsumed sulfur vapor indicate that the furnace is too hot, probably from the use of too much air, and that there is danger of sublimation.

Attached to, or immediately adjoining, nearly every type of sulfur burner is a combustion chamber which the gas enters as soon as it leaves the burner proper. This is so arranged that more or less air can be admitted at will through appropriate dampers, and in this way sublimed sulfur carried along from the burner can be completely burned to sulfur dioxide.

The burning of pyrites in burners of the old type was considerably more difficult to control than the burning of sulfur, and it could be worked advantageously only where the burners could be grouped together in sufficient numbers to insure gas of even composition. Many of these difficulties have been overcome by modern mechanical furnaces, of which the Herreshoff furnace, shown in Fig. 26, is a type. These burners usually have five shelves over which the pyrites is raked in succession by mechanically operated rakes. The shafts and arms are hollow and are cooled by a current of air supplied by a fan; part of the hot air thus produced is used in the lower parts of the chamber and materially assists combustion. The heat produced by the oxidation of the sulfur and iron is sufficient for carrying on the operation, and once the furnace is in good working condition no fuel is required. The spent pyrites or cinders leave the furnace with $\frac{1}{2}$ per cent to 4 per cent of sulfur. The separation of dust is particularly important where pyrites are used. This was formerly done by passing the gas through long chambers of large area so that the velocity of the gas would be slight. In modern practice it is more successfully accomplished by passing the gas through towers into which water is sprayed; this not only removes dust but also takes out SO_3 and cools the gas. Provided the wash water is discharged at 175° F. (80° C.) the loss from dissolved SO_2 is very slight.

In the Nichols-Freeman[43] flash-roasting system, developed in Canada, the pyrites is first ground in a ball mill and blown with preheated air into a combustion chamber and waste-heat boiler. The gas is cooled and scrubbed by passing it through a tower which is filled with

stoneware and into which water is sprayed at the top.   This method is claimed to give a more complete combustion of the pyrites, a higher SO_2 content in the gas, and the generation of steam from waste heat.

The gas from sulfur burners operating under satisfactory conditions generally contains 14 to 20 per cent of SO_2 by volume; the maximum which it can possibly contain is 21 per cent.   In the case of pyrites the theoretical maximum is 16.2 per cent of SO_2, and it generally runs
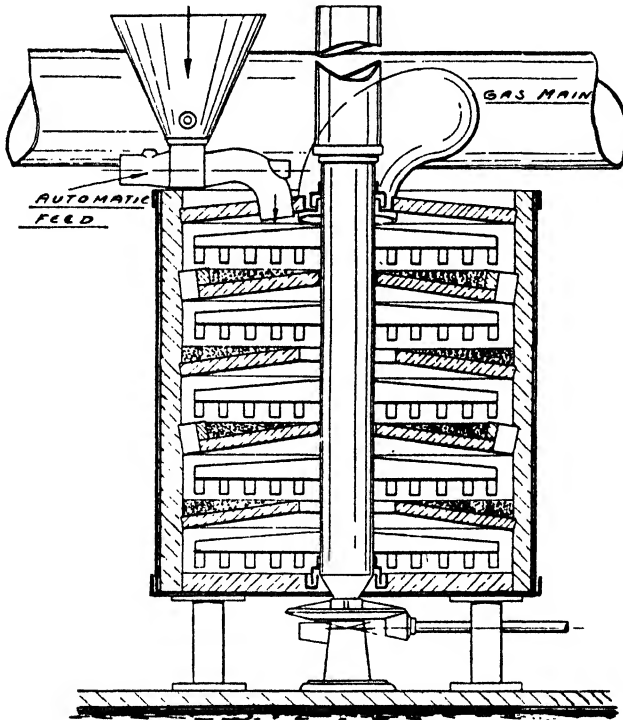
FIG. 26.   HERRESHOFF PYRITES BURNER.

about 10 to 14 per cent.   As a rule when burning sulfur about 2 to 3 per cent is converted into SO_3 while with pyrites as much as 13 per cent may be lost in that way.

After leaving the combustion chambers the gas is conveyed through iron pipes to the coolers.   Up to this point the gas is hot and dry and has little action on iron, but for the cooler and all pipes beyond lead should be used.   The cooler generally consists of pipes through which the gas passes back and forth.   These pipes are placed in a trough through which water flows, or are so arranged that a thin film of water

trickles over them. The cooling surface should be about 15 square feet per ton of daily production, which is sufficient to bring the gas nearly to the temperature of the water in summer. In winter the gas should be cooled to about 55° F. (12.8° C.). Regular and uniform cooling of the gas is very important as the rate of absorption and the quantity of gas dissolved depend very largely upon the temperature. Table 26[5] presents the vapor pressures of sulfur dioxide solutions at different temperatures.

TABLE 26

VAPOR PRESSURES OF SULFUR DIOXIDE SOLUTIONS

Temperature in °C.	Total Pressure in Centimeters of Hg; Concentration in Per Cent SO_2					
25	Pressure 10.8	18.4	29.3	41.4	63.5	70.9
	Concentration 1.16	2.25	3.36	4.34	6.66	7.40
30	Pressure 13.0	23.2	35.7	48.7	75.5	84.5
	Concentration 1.15	2.24	3.34	4.31	6.62	7.36
40	Pressure 19.4	34.8	50.0	67.4	102.2	116.5
	Concentration 1.14	2.21	3.29	4.24	6.53	7.28
50	Pressure 28.1	48.7	68.2	90.7	135.0	153.6
	Concentration 1.12	2.17	3.24	4.16	6.45	7.19
60	Pressure. 39.6	65.4	90.6	118.6	173.3	197.7
	Concentration 1.11	2.14	3.19	4.08	6.35	7.12
70	Pressure 54.0	87.3	117.6	150.2	218.9	249.4
	Concentration 1.09	2.10	3.14	4.00	6.24	7.02
80	Pressure 73.2	113.2	148.7	188.1	270.3	308.3
	Concentration 1.07	2.06	3.06	3.91	6.14	6.92
90	Pressure 97.1	114.5	186.6	231.8	329.	
	Concentration 1.05	2.02	3.00	3.81	6.03	
100	Pressure 127.5	182.5	230.8	280.1		
	Concentration 1.03	1.97	2.93	3.72		
110	Pressure 166.3	230.0	283.	338.		
	Concentration 1.01	1.93	2.87	3.63		
120	Pressure 213.	284.5	344.			
	Concentration 1.00	1.89	2.82			

Liquid Sulfur Dioxide. There have been various proposals to use liquid sulfur dioxide in the preparation of cooking liquor, as well as in other ways in the process. For liquor making it has a number of obvious advantages, such as the elimination of sulfur storage and burning and the use of coolers, and it would permit a cool gas, free from SO_3, to be supplied to the absorption system. Edwardes[23] considered these and other advantages to be great enough so that it would pay to purchase it at $15 per ton as against $24 per ton for sulfur, both f.o.b. mill.

McKee and Cable[62] conducted experiments on the extraction of rosin from longleaf pine by means of liquid sulfur dioxide, and the subsequent cooking of the chips with ordinary sulfite liquor. Good results were obtained with sapwood, but those with heartwood were not entirely satisfactory.

Absorption Apparatus. The apparatus for preparing the bisulfite solution is of either of two types, depending upon the form in which the lime is handled. Milk-of-lime systems are used for hydrated lime in suspension; limestone towers handle limestone lumps of considerable size. Since the limestone tower is perhaps the oldest, the simplest, and the most widely used type, it will be described first.

The tower first used by Mitscherlich was cylindrical in form and built of wood. Water was introduced at the top of the limestone-filled tower and sulfur dioxide gas at the bottom, reacting with the limestone. The carbon dioxide formed and unabsorbed sulfur dioxide gases passed off at the top. It was later found advantageous to taper the towers, making them slightly larger at the bottom to permit settling of the limestone without arching. Modern towers are constructed of reinforced concrete lined with acid-resisting tile. Mitscherlich towers vary from 6 to 10 feet in diameter and from 100 to 150 feet in height. Frequently four or more towers are built together and the whole surrounded with a structure with stairs, platforms, and stone hoist. A water tank, supplied with cold water, surmounts each tower. The stone is supported on strong oak beams placed about 6 to 10 feet from the bottom. Below these, and about a foot above the acid outlet, are other beams set close together to catch pieces of stone which pass the upper timbers. Frequently the tower is divided into sections by timber gratings to assist in the filling and the regulation of the absorption. Some towers act as chimneys and no artificial draft is necessary; with others it is desirable to place a fan between the burners and the towers and a steam exhaust at the top of the towers.

Ritter-Kellner towers are constructed in pairs; the acid from the bottom of one is pumped to the top of the second while the gas from the top of the second is led into the base of the first. These towers are smaller than the Mitscherlich towers and have the advantage of avoiding undue loss of gas. This is essentially the principle of the Jenssen system, which has been widely adopted in America. In this system the two towers are cross-connected in such a way that either can be used for making strong acid, while the other serves to absorb the gas not taken up by the first.

Further development along this line is the multiple-tower system where towers about 20 feet high are worked in groups of six to eight.

The acid passes through these in succession in one direction and the gas in the other. The multiple-tower system permits a fairly close control of the temperature and acid composition but is somewhat expensive to maintain and operate. In European mills the tendency has been to use fewer and larger towers.

In all these systems the towers are filled with lumps of limestone or dolomite. In European mills a special soft limestone is preferred, but sufficiently pure material of this nature is not available in this country and ordinary dense stone is used. A stone low in magnesia and as free as possible from dirt, iron, and silica is preferred. Since marble is practically all calcium carbonate and is of uniform structure, it is highly satisfactory for use in towers. A typical analysis of a suitable stone is as follows:[18]

	PER CENT
Loss on ignition	43.63
Iron and alumina	0.74
Calcium oxide	54.10
Magnesium oxide	0.82
Silica	0.59
	99.88

The water is discharged over the stone at the top by spray pipes or some similar device and in passing downward forms a thin film on the surface of the lumps. The gas from the burners enters the base of the tower under the grating and passing upward over the moist limestone is very rapidly absorbed by the downward-flowing film of water. In the lower part of the tower crusts of sulfate or of monosulfite of lime sometimes almost stop the flow of gas; the latter is particularly liable to form if the gas is weak or insufficient water is used. Irregular acid is also likely to result if the temperature varies since, as already shown, the solubility of the gas decreases rapidly with rise of temperature while at the same time the base is much more quickly dissolved, thus changing the proportion between free and combined acid.

Equilibrium data for conditions prevailing in limestone towers and application of the theory of absorption to their design and operation are discussed by Beuschlein and Conrad.[10]

Although several different milk-of-lime absorption systems have been in use in America, the Barker apparatus, illustrated in its relation to the other equipment in Fig. 27, may be considered typical. The construction of the tower is shown in Fig. 28. It is a high tank divided into three or more compartments by horizontal, perforated partitions. The milk of lime enters the upper compartment in a continuous flow and
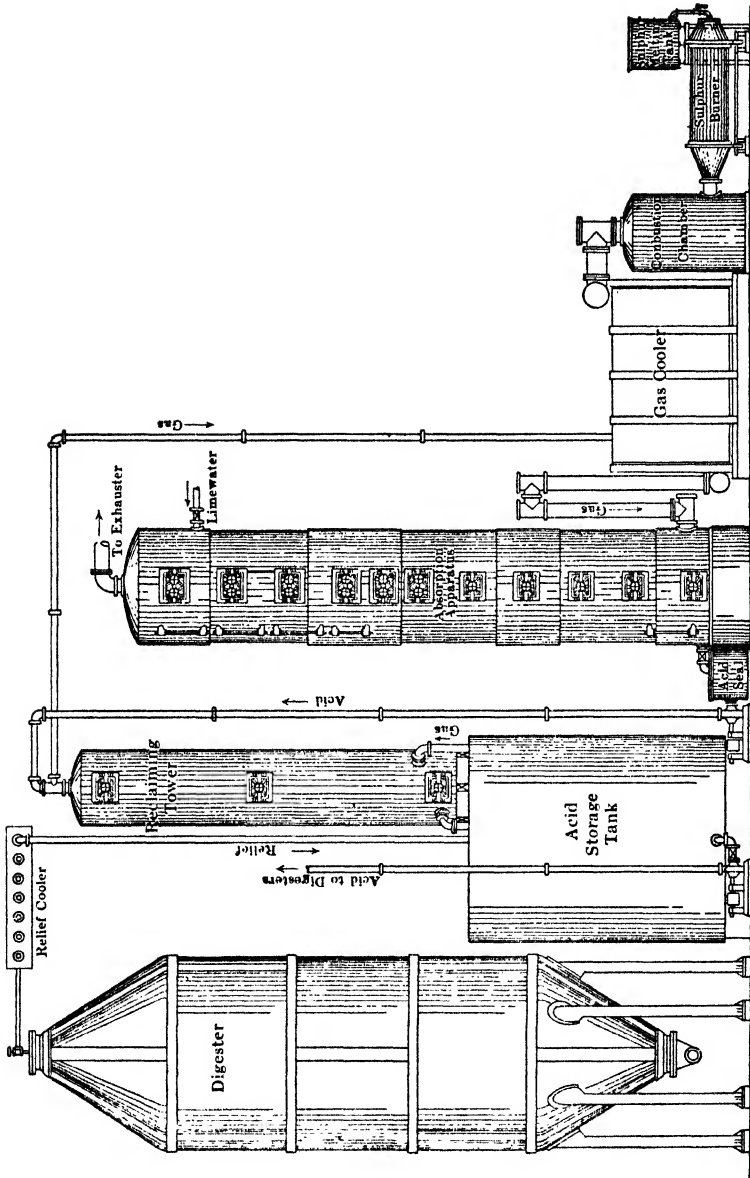
FIG. 27. BARKER ACID TOWER IN RELATION TO OTHER EQUIPMENT.
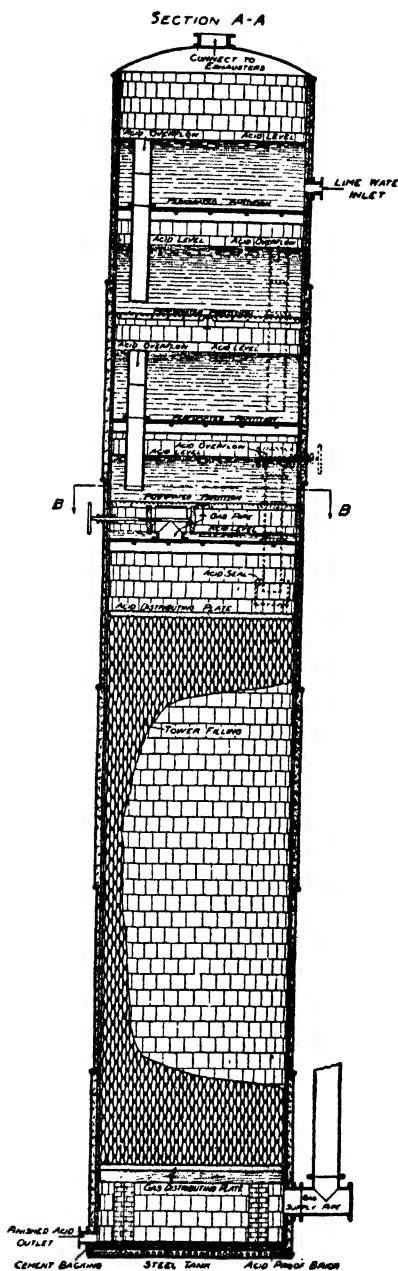
FIG. 28. BARKER TOWER, SECTIONAL VIEW.

meets the gas bubbling up through the perforated false bottom. The weak liquor passes through an overflow pipe to the next compartment, where it absorbs more gas, and so on through the four sections. From the lowest one it flows onto a distributing plate which allows it to trickle down into the absorbing tower where it is strengthened by entering gas to the desired composition.

The quality of the lime used for milk-of-lime absorption systems is important. Its value is very often considered to increase with the amount of magnesia it contains. It should be well burned, should slake easily, and should be as free as possible from silica and iron. Air-slaked or poorly burned limes are less reactive than those of good grade and are likely to be of variable composition, which may be reflected in the composition of the acid. The analyses in Table 27 show the composition of several extensively used limes from different parts of the country.

Although it is customary to use dolomite, high-calcium lime can be employed in the Barker system without difficulty.

Lime for the absorption system is first slaked either in tanks provided with agitators or in troughs. One authority recommends a tank with a perforated plate on which the lime is dumped after filling the tank with water to 1 inch above the surface of the plate. The lime is sprinkled on top with water and

TABLE 27

	Massachu-setts	Ohio	New Brunswick
	Per cent	Per cent	Per cent
Calcium oxide, CaO..................	56.02	58.61	55.96
Magnesium oxide, MgO..............	40.10	40.25	37.98
Alumina and ferric oxide, Al_2O_3 and Fe_2O_3...........................	0.57	0.12	1.23
Sulfur trioxide, SO_3.................	0.11	0.15	0.16
Insoluble in HCl, sand, etc...........	0.94	0.07	1.51
Silica soluble in acid, SiO_2...........	0.47	0.15	1.81
Loss on ignition, H_2O, CO_2, etc........	1.43	0.51	1.00
	99.64	99.86	99.65

when it steams freely is quickly covered with water. The milk of lime produced is diluted sufficiently so that it can be strained through brass sieves of 60 meshes to the inch and the strained material run to storage tanks fitted with agitators where it is diluted to the proper consistency. The milk of lime must be cold when it goes to the absorption system. According to Beveridge,[11] the finished milk of lime has a specific gravity of 1.0075 and contains 6.31 grains per liter of CaO and 4.19 grams per liter of MgO. This corresponds to about 91 pounds of lime of the composition given to 1000 gallons of acid. As the lime is never entirely dissolved and some is lost as sulfate and monosulfite in cleaning the apparatus, more than the above quantity has to be used, the amount depending on the quality of the lime, the type of apparatus, etc.

Milk-of-lime systems are no longer common in Europe, where towers are generally employed, but they are still used to some extent in America. The tower systems are claimed to be somewhat simpler to operate, to require less power, and to cost less for upkeep. The cost of the unburned stone for the towers is less than that of the burned lime for making the milk of lime. On the other hand, milk-of-lime systems are generally considered to be more satisfactory for dolomite lime.

The losses which occur in making sulfite liquor are those due to dirt, ash, and moisture in the sulfur, to sublimation, and to the formation of sulfuric acid. The loss from the first four causes should never exceed 5 per cent, but that from formation of sulfuric acid is likely to amount to very much more unless careful control is maintained. The formation of monosulfite, which is removed with the sediment in the storage tanks or in cleaning the absorption system, may also cause considerable loss. Such wastes should be examined before being thrown away as it often pays to work them over. There are also losses of lime from

unburned cores and screenings in the milk-of-lime system, and from
sludge and undissolved fragments in the tower system. If the lime is
not of the right type such losses may be very considerable.

The acid made in either the tower or the tank system varies widely
in different mills. There is no essential difference, however, between
the two systems with regard to the liquor produced. The acid before
being enriched by the recovered gas generally has the following
composition:

	PER CENT
Total SO_2	2.5 to 3.5
Free SO_2	1.6 to 2.2
Combined SO_2	0.9 to 1.3

The finished acid when ready for the digesters is also very variable in
strength. From reports on a number of American mills the figures in
Table 28 have been selected as representative. Acid of the strength of

TABLE 28

	1	2	3	4	5
	Per cent	Per cent	Per cent	Per cent	Per cent
Total SO_2......	4.30	4.09	5.50	3.80	6.24
Free SO_2.......	3.10	2.46	4.50	2.40	5.22
Combined SO_2...	1.20	1.63	1.00	1.40	1.02

sample 5 can be obtained during warm weather only by employing
artificial refrigeration or by means of auxiliary absorption towers
operating under pressure. Milk-of-lime absorption systems can oper-
ate under pressure by employing a compressor to force the gas through
the suspension rather than inducing its flow by means of a vacuum
pump. Sulfur dioxide absorption data applicable to the design of
absorption towers are given by Reiley.[78]

Nature of Base Used. It has already been stated that for tower sys-
tems the lime should be low in magnesia, but that for milk-of-lime
systems it should contain much magnesia. Since the liquor from either
system is used for the same type of pulp it naturally brings up the
question whether the kind of base used is of much importance. From
small-scale experiments Cable[15] concluded that with spruce wood the
yield was the same whether the base was calcium, magnesium, sodium,
or ammonia. The fiber cooked with sodium base bleached slightly
easier. It has been long held in practice that pulps from high-
magnesium-base digestions have more pliable fibers than those from
straight calcium-base digestions.

Experiments at the United States Forest Products Laboratory[58] show slight advantages in yield, strength, and bleach requirement of pulps made from spruce and other woods commonly used for sulfite pulp with sodium-base liquor over those made under similar conditions with calcium-base liquor. Greater differences were found in cooking jack pine and Douglas fir in that reasonably complete reduction was obtained with sodium-base liquor whereas calcium-base liquor resulted in a high percentage of screenings owing to difficulty in cooking the heartwood completely. Another advantage of the sodium base resulting from its greater solubility is the possibility of using a higher concentration of combined sulfur dioxide in the liquor. Increasing the combined sulfur dioxide up to the point where all the sulfur dioxide is present as bisulfite improved the yield and quality of the pulp. Use of neutral sodium sulfite liquor gave remarkably strong, light-colored, bleachable pulps from a wide variety of species.

Liquor Storage and Pumping. Storage tanks for liquor are generally of wood, either southern pine or Douglas fir heartwood, without lining. They should be made tight with water or steam before any liquor is admitted, so that no monosulfite may crystallize between the staves, and the top should be kept covered with water to prevent drying. When the liquor is stored in quantity there is little loss in strength either through escape of gas or oxidation to sulfate. The tanks should be fitted with gage glasses to show the depth of liquid, and the delivery pipes should draw from near the bottom but high enough to avoid sediment. The tanks should be so located that the sediment may be easily washed out when necessary.

The acid in storage should be warm in order to save steam in cooking. According to Kraske,[55] each increase of $1°$ C. in the temperature of the acid at the start means a saving of about $1\frac{1}{2}$ per cent of the steam required. For acid in wood tanks $36°$ C. is safe, but if the temperature rises to $40°$ C. or above, the pitch tends to work out of the staves and the life of the tank is shortened.

The best method of transferring the liquor from the storage tanks to the digesters is by means of a rotary pump of acid-resisting bronze placed so that the liquor flows to it under a small head. When the pump is so placed that a foot valve is necessary on the suction pipe, trouble is likely to be caused by crystallization of monosulfite in the working parts.

Digesters and Digester Linings. The acid liquor used in the sulfite process acts so destructively on iron that some form of lining is necessary to protect the digester shell.

Lead satisfactorily resists the action of the acid liquor owing very

largely to the formation of a surface film of insoluble lead sulfate which acts as a protective coating for the metal beneath. Lead, however, has certain properties which have prevented its successful use in digester lining in spite of many attempts. Its coefficient of expansion is more than twice that of iron, and after it has been expanded by heat it does not return to its original size on cooling, so that " crawling " and " buckling " result, and cracks are likely to appear in short turns. Also, there is a gradual creeping downward of the lead in vertical digesters, causing the upper part to stretch out and finally give way. Uniting the lead to the iron by melting it on over a flux of zinc chloride has likewise been unsatisfactory.

Bronze digesters, built of cast sections, were tried at one time but were found to be attacked by the liquor with the formation of black scales of oxide and sulfide of copper. Heating to the temperatures used in cooking considerably reduces the strength of bronze, and after several disastrous explosions the use of such digesters was abandoned.

The Salomon-Brüngger digester consisted of an inner shell of welded steel and an outer shell also of steel but riveted. The protective coating was obtained by admitting sulfite liquor into the digester, which had been previously heated by steam in the jacket at about 40 pounds pressure. This treatment caused the deposit of a hard, impervious crust of sulfite of lime which gradually increased in thickness with each succeeding cook. This coating did not give adequate protection, and the method was never in extensive use.

The Mitscherlich lining is interesting as being the first in which bricks were used. It consists first of a coating of tar and pitch applied directly to the shell, then a thin lining of sheet lead with the edges burned together, and finally two courses of dense vitrified bricks with tongues and grooves. These were sometimes laid in Portland cement.

The Preston lining consists of bricks of Scottish clay backed with a mixture containing clay and lead mixed to the consistency of bread dough with silicate of soda. This must be applied to a perfectly clean shell.

Modern digester linings are generally of acid-proof bricks backed with cement next to the shell. The bricks are 2 to 3 inches thick, and the cement backing is about an inch thick. Sometimes a lead lining is applied next the shell and upon this the cement backing is laid. This is seldom done, however, as it is customary to pierce the digester shell with numerous small telltale holes so that the approximate location of cracks in the lining may be known. The cement for the backing and for pointing the first layer of bricks varies more or less in different localities. Steffanson[96] gives its composition as 1 part of cement and 2 parts

of crushed and sifted acid-proof brick with enough asbestos added to render it non-brittle; this is mixed to the desired consistency with 4° Bé. silicate of soda. The last layer of bricks is pointed with litharge and glycerine, and the bricks should be set half an inch apart to make repairs easy. Another formula for pointing the inner layer of bricks is 5 parts litharge, 2 parts cement, and 3 parts quartz sand, all measured by volume. After these materials are mixed dry, they are moistened with glycerine to the right consistency for use. This should be mixed in small quantities only and used quickly, as the mixture retains the proper consistency for only a short time. Digesters pointed with this mixture have been operated up to 18 months without repairs, and in some of them the pointing has proved more durable than the bricks so that the latter have worn down, leaving a raised network of cement exposed.

The bricks for digester lining should be very hard, dense, and well annealed. If soft or underburned they are likely to crack from changes in temperature and pieces then come away in the pulp. When tested by immersing in water for 24 hours they should not absorb more than 2 per cent of their weight.

Since the development of stainless steels resistant to corrosion by sulfite liquor, experimental digesters have been constructed of these materials and also of carbon-steel plate to which a thin lining of stainless steel is attached. With improvement in the methods of fabrication, application of the latter to commercial-size digesters appears to be a possible future development.

Stainless steels, although more expensive, have now largely replaced copper and bronze for digester pipe and fittings owing to their greater corrosion resistance. Miller[63] shows this trend in a survey of materials used in sulfite-mill construction and gives in detail the alloys for different purposes.

The general form of digester is a vertical cylinder with conical or dome-shaped top and conical bottom. The total length is about three times the diameter, and the lower cone is about 60°. Digesters of other forms are, of course, found in some of the older mills and horizontal digesters are sometimes used for the Mitscherlich process. The size of digesters has gradually increased; formerly a capacity of 4 tons of fiber per charge was considered large but now 18 tons or more is not uncommon. Table 29[106] gives the approximate capacities of sulfite digesters of standard construction and lined with the usual brick and cement lining. Digesters of type A have bottom cones of 52° and domes with a radius exceeding the radius of the cylinder; those of type B have conical domes as well as lower cones.

TABLE 29

Digester Capacity

Length of Digester in Feet	Cubic Feet Inside Shell	Cubic Feet Inside Lining (Lining thickness in inches)				Cubic Feet Inside Shell	Cubic Feet Inside Lining (Lining thickness in inches)			
		5½	6	7½	8		5½	6	7½	8
		Type A					Type A			
		10-foot diameter inside shell					12-foot diameter inside shell			
55	3,752	3,042	2,982	2,803	2,744	5,232	4,386	4,311	4,094	4,016
50	3,359	2,718	2,664	2,502	2,449	4,667	3,903	3,836	3,640	3,569
45	2,966	2,394	2,346	2,201	2,154	4,101	3,421	3,361	3,186	3,123
40	2,574	2,070	2,028	1,901	1,859	3,536	2,939	2,886	2,732	2,676
35	2,181	1,746	1,710	1,600	1,564	2,970	2,456	2,411	2,279	2,229
30	1,788	1,422	1,392	1,299	1,269	2,405	1,974	1,935	1,825	1,782
25	1,395	1,098	1,074	999	974	1,839	1,491	1,460	1,371	1,335
		14-foot diameter inside shell					15-foot diameter inside shell			
55	6,912	5,932	5,847	5,595	5,510	7,923	6,869	6,777	6,502	6,411
50	6,142	5,260	5,183	4,956	4,880	7,039	6,090	6,007	5,759	5,678
45	5,372	4,588	4,520	4,318	4,250	6,156	5,312	5,237	5,017	4,944
40	4,602	3,916	3,856	3,680	3,628	5,272	4,533	4,467	4,274	4,211
35	3,833	3,244	3,192	3,041	2,990	4,389	3,754	3,698	3,532	3,477
30	3,063	2,571	2,529	2,403	2,360	3,505	2,975	2,928	2,789	2,744
25	2,293	1,899	1,865	1,764	1,730					
		16-foot diameter inside shell					17-foot diameter inside shell			
65	10,760	9,403	9,270	8,928	8,813	12,102	10,691	10,566	10,197	10,077
60	9,754	8,509	8,388	8,073	7,968	10,967	9,676	9,561	9,223	9,113
55	8,749	7,616	7,506	7,219	7,123	9,832	8,660	8,556	8,248	8,149
50	7,744	6,722	6,624	6,364	6,279	8,697	7,644	7,550	7,274	7,185
45	6,738	5,829	5,742	5,510	5,434	7,562	6,628	6,545	6,300	6,222
40	5,733	4,936	4,860	4,656	4,589	6,428	5,612	5,540	5,326	5,258
35	4,728	4,042	3,978	3,801	3,744	5,293	4,597	4,534	4,352	4,294
		18-foot diameter inside shell					19-foot diameter inside shell			
65	13,448	11,950	11,817	11,424	11,296	14,773	14,235	13,062	12,648	12,513
60	12,176	10,804	10,682	10,323	10,206	13,355	12,817	11,789	11,410	11,287
55	10,904	9,658	9,547	9,221	9,115	11,937	11,399	10,517	10,173	10,061
50	9,631	8,512	8,412	8,119	8,024	10,520	9,982	9,245	8,936	8,836
45	8,359	7,366	7,277	7,017	6,933	9,102	8,564	7,972	7,699	7,610
40	7,087	6,220	6,143	5,916	5,842	7,685	7,147	6,700	6,461	6,385
35	5,814	5,074	5,008	4,814	4,751	6,267	5,729	5,428	5,224	5,159
		Type B					Type B			
		12-foot diameter inside shell					14-foot diameter inside shell			
50	4,598	3,843	3,778	3,587	3,533	5,825	4,973	4,899	4,678	4,605
45	4,032	3,360	3,303	3,133	3,086	5,056	4,301	4,235	4,039	3,975
40	3,467	2,878	2,827	2,679	2,639	4,286	3,629	3,571	3,401	3,345
35	2,901	2,396	2,352	2,225	2,192	3,516	2,957	2,908	2,763	2,715
30	2,336	1,931	1,877	1,771	1,745	2,746	2,284	2,244	2,124	2,085
		15-foot diameter inside shell					16-foot diameter inside shell			
60	8,590	7,458	7,360	7,063	6,964	9,565	8,439	8,255	7,941	7,838
55	7,706	6,679	6,591	6,320	6,231	8,560	7,536	7,372	7,086	6,994
50	6,822	5,900	5,821	5,578	5,497	7,555	6,632	6,488	6,232	6,149
45	5,939	5,121	5,051	4,835	4,764	6,549	5,729	5,605	5,378	5,304
40	5,055	4,342	4,282	4,093	4,030	5,544	4,826	4,721	4,523	4,459
		17-foot diameter inside shell					18-foot diameter inside shell			
65	11,415	10,064	9,945	9,587	9,470	13,233	11,731	11,598	11,204	11,075
60	10,280	9,048	8,940	8,612	8,506	11,961	10,585	10,463	10,102	9,985
55	9,145	8,032	7,935	7,637	7,542	10,688	9,439	9,328	9,000	8,894
50	8,011	7,016	6,930	6,662	6,578	9,416	8,293	8,193	7,898	7,803
45	6,876	6,001	5,925	5,687	5,614	8,144	7,147	7,056	6,797	6,712

The digester space required to produce 2000 pounds of dry pulp is given by Steffanson as follows:

	CUBIC FEET
Mitscherlich process	400–425
Quick-cook process	450
For easy bleaching pulp	475–500

Cooking. The method of making a cook depends on whether the Mitscherlich or the quick-cook process is being employed. The Mitscherlich is very generally used in Europe but in America is not nearly so common as the quick-cook or Ritter-Kellner process.

In the Mitscherlich process the digesters are either horizontal or vertical stationary digesters. All the cooking is done by steam admitted to coils of hard lead, copper, or stainless-steel pipe placed in the bottom of the digester. The standard procedure is to fill the digester with chips and then steam gently for several hours with direct steam, the water condensing being allowed to run to waste as a brownish liquid. Care must be taken during this period to avoid steam pressure in the digester as temperatures much in excess of 100° C. are likely to burn the wood. After steaming, all valves except that leading to the liquor tanks are closed and the partial vacuum formed by the cooling of the digester and the condensation of the steam draws the cold liquor in rapidly. The object of this steaming and subsequent admission of cold liquor is to obtain thorough penetration of the chips by the liquor and so prevent floating and burning. Steam is now admitted to the coils and the temperature raised to 110° C. as rapidly as possible, although this may require as much as 12 hours because of the large size of the digester. When pressure is reached it is relieved by opening a valve for a few minutes to get rid of air; this is repeated two or three times in the next hour. Since the relief from Mitscherlich cooks contains no liquor no separator is necessary, and the relieved gas can go at once to the reclaiming system. The temperature in the digester is gradually raised to about 120° C., which is maintained throughout the cooking period; during this time the pressure should not exceed 80 pounds. About an hour before the end of the cook the steam is shut off and the pressure gradually reduced by relieving gas. The liquor is then blown out and the digester filled with water. After draining and filling with water again the pulp is washed out through the bottom openings.

The liquor used in the Mitscherlich process is about 3.5 to 4.5 per cent total SO_2 with 0.9 to 1.24 per cent combined. The steam used in the coils is at 60 to 100 pounds pressure; 75 pounds in the coils gives about

90 pounds in the digester. The actual cooking time varies in different mills, usually being from 20 to 30 hours, depending on the temperature employed. It was originally about 80 hours, but this has been greatly reduced by raising the temperature of cooking and by using some direct steam to bring the charge up to pressure quickly. In this latter case space must be left in the digester to allow for condensation.

In modern European practice the actual cooking time varies from 12 to 22 hours, the complete cycle being about 6 to 7 hours longer than that. For two different mills Klein[51] gives the time required by the different operations as in Table 30.

TABLE 30

	Mill 1	Mill 2
	Hours	Hours
Filling of chips...................................	1	1½
Steaming..	1	2
Pumping in acid..................................	¾	1
Cooking...	10½	14½
Blowing off gases and lyes........................	1½	¾
Washing and emptying............................	¾	¾
Cleaning and repairs..............................	1	½
Total.....................................	16¼	21

Many of the mills which make the most uniform and reliable product handle each cook as though it were a separate process, titrating the cooking liquor from time to time and regulating the temperature correspondingly in accordance with previously observed results.

The particular advantages of the Mitscherlich process are strong fiber and high yield because of the comparatively weak acid and the low temperature of cooking. According to Klein it also has the advantage of about a third more yield per cubic foot per cook than American practice in the quick-cook process.

The quick-cook process in which the steam is blown directly into the digester is most general in this country. This method as followed for many years in America will first be described. Modifications, including the use of hot acid, forced circulation, and indirect heating, will be described later. According to Genberg,[29] this method was derived from the Ritter-Kellner process but is in many respects quite different. In the Ritter-Kellner process, as in the Mitscherlich, the gassing of the digesters, liquor draining, washing of the pulp in the digesters, and dumping are characteristic, while steaming and refilling with chips are practiced only in the Mitscherlich process and blowing

of the entire digester charge is done only in the quick-cook method.   In the quick-cook method the digester is filled with chips by allowing them to drop into the digester.   This results in a rather loose packing, and the settling during the first part of the cook suffices to cover them completely with liquor.   Mechanical chip distributors, which effect a closer packing, are now often used to increase the amount of chips charged and the yield per digester.   These devices consist of rotating paddles or other types of deflectors placed below the neck of the digester, or they blow steam or air into the stream of chips as they enter the digester.   Sometimes it is necessary to increase the strength of the liquor to provide for the increased amount of wood.   Charging the acid into the bottom of the digester is the most generally satisfactory method.   It saves some time since the introduction of acid may be started before the digester is completely filled with chips, it prevents loss of sulfur dioxide, and it may aid circulation to some extent.   Steam for cooking is introduced through a pipe opening into the bottom of the cone and also, in many mills, through nozzles near the top of the cone directed upward to give a better distribution.

The steam for cooking may be superheated or ordinary saturated steam.   Superheated steam, if not hot enough to cause too much over-heating at the inlet, affords certain advantages from less dilution of the liquor.

The steam required for cooking is much greater than for a soda cook of a corresponding number of cords.   This is due to the continual relief of gas and steam through the coolers into the recovery system. Andrews[3] calculates the saturated steam for a 14 by 47 foot digester holding 16 cords of rossed wood as about 60,000 pounds per cook.   In another plant with digesters of about the same capacity, steam flow meter records over a period of a year showed the daily average steam consumption per cook to vary from 54,000 to 97,000 pounds.   The minimum was in August, and the maximum occurred in February. These figures correspond to about 3.4 to 6.0 pounds per pound of fiber. However, the heat recovery obtained with the hot acid systems, now common, reduces this figure to 2.0 to 2.5 pounds of steam per pound of pulp.   Alfthan[1] claims for the Ritter-Kellner process 2.4 pounds of steam per pound of cellulose.   Of this about 70 per cent is used in heating from 26° to 105° C. and 30 per cent in digesting from 105° to 140°.   Berger[7] states that European practice is often as low as 2.8 pounds as compared with American records of 4 to 4½ pounds of steam per pound of fiber, and Klein[51] states that Scandinavian mills need only 1.8 to 2.0 pounds of steam for cooking a pound of strong sulfite by the indirect process.

In steaming a cook it is very important that the pressure be brought up slowly as otherwise a high temperature may be reached before the liquor has had time to penetrate the chips, and their centers will be hard and red or brown in color. The time from the start until 75 pounds pressure is reached varies in different mills from 2 to 4 hours. The pressure, however, does not afford a reliable indication of conditions within the digester since the actual steam pressure is augmented by that of the gas set free during cooking, and in some cases the indicated pressure may be almost wholly hydrostatic owing to the filling of the digester by condensation. The temperature is therefore the real factor to be watched. It should be taken one-third of the way down the digester if a single thermometer is used. Thermometers are also often located near the top and bottom of the cylindrical portion of the digester to indicate temperature variations in the different portions and to check the effectiveness of circulation. The best method of keeping track of the temperature is by means of some form of recording thermometer, as this gives a permanent record of each cook.

Miller[64] has shown that, at a temperature over 100° C., SO_2 alone will alter lignin so that it will not dissolve. Since the acid portion penetrates the chips faster than the bisulfite part it is important to have thorough penetration of all portions of the liquor before the critical temperature of 110° is reached. For dry white spruce chips, ¾ inch long, this will require 1½ hours; for wet chips a half hour more will be needed. For hemlock chips a slightly longer time is required.

Allen[2] claims that the rate of steam admission to the digester is the important factor in cooking and that temperature records do not show how fast steam is being supplied. He has worked out an automatic control system consisting of a power-driven steam valve electrically connected to a steam-flow meter on the digester steam line. A copper plate with an insulated hole fits over the spindle of the steam-flow meter clock, and the form of this plate determines the rate of steaming and hence controls the cooking. This rate can be varied easily by means of different plates to suit the desired conditions. An automatic relief valve of diaphragm type working against a spring, and relief strainers which do not plug, are parts of this system.

Although automatic methods of controlling the temperature have been found satisfactory with forced circulation of the liquor, their application to the ordinary direct-cook process has been more difficult owing to a time lag and variation of temperature in different parts of the digester. Methods of temperature and pressure control in present use are principally of two types. In one method steam is introduced at a rate to give the desired temperature schedule and the digester

pressure is then controlled automatically by operating the relief valve. In the other method the digester pressure is controlled automatically by opening or closing the steam valve. The relief valve is manually operated to follow the desired temperature schedule; as the relief valve is opened, the steam valve also opens to maintain the digester pressure.

No hard and fast rule for cooking can be given; each mill has its own particular method which is generally the result of gradual evolution and is based on its particular requirements. As an example of the procedure in cooking easy-bleaching pulp of high quality Steffanson[96] gives the following schedule: Steam in such a way as to reach 75 pounds pressure in 2 to 3 hours; open relief and bring temperature to 240° F. (115.5° C.) in about an hour. Close both steam and relief valves for $1\frac{1}{2}$ hours, then turn on steam and open relief very slightly The maximum temperature of 300° F. (149° C.) should be reached in 10 hours with the maximum pressure still 75 pounds. Now shut off steam but not relief, allow the pressure to drop to 50 pounds in 1 to 2 hours, and discharge into the blow pits. At the end of the cook the liquor should test 0.05 per cent total SO_2. If the cook is blown at a pressure much in excess of 50 pounds some partially cooked chips will be blown to pieces and cause shives.

In another mill making an easy-bleaching sulfite for use in writing papers the following schedule is in effect: Steam in such a way that the temperature will be 228° F. at the fourth hour; 246° at the fifth; 262° at the sixth; 278° at the seventh; 290° at the eighth; and 298° at the ninth hour. Start to reduce pressure when 5 cc. of liquor require 2.7 cc. of 0.1 N iodine and lower to 50 pounds at blow, which is when 5 cc. of liquor require 0.7 cc. of iodine.

In summarizing the results of studies at the Forest Products Laboratory of the temperature schedule in sulfite cooking, Swanson[100] says that the digester should be heated rapidly to the critical temperature (about 110° C. for spruce and 120° C. for hemlock), the rate of temperature rise being limited by the time necessary for thorough penetration of the chips by the liquor. For high yields of strong bleached or unbleached pulp the temperature should be raised from the critical point to the maximum at a uniform rate or, preferably, allowed to follow an upward curve gradually increasing in steepness as the maximum is reached. The maximum temperature should be as low as is consistent with the time available for cooking. When digesters are operated at the pressures commonly used, temperatures in excess of 150° C. (302° F.) are inadvisable because of the low content of sulfurous acid above that point left in the digester for carrying out the desired pulping action.

Figure 29 shows the general method of recording the conditions within the digester during the cook. Observations are taken at frequent intervals and plotted on the chart in such a way as to show the gage, gas, and steam pressures. This gives a graphic representation which can be followed easily by the workmen. The chart given is for a quick-cook easy-bleaching sulfite. Figure 30 is the temperature record taken during such a cook.

During the progress of a cook the steam added and the chemical reactions taking place within the digester cause more or less gas to be evolved, which results in a gradual building up of the pressure. This gas pressure is not injurious to the fiber, but it is the general custom to reduce it by " relieving " or blowing off some of the gas either at intervals or continuously in order to operate the digester at a safe working pressure, to aid circulation in the digester, and to make recovery of the SO_2 more efficient. Study by Schwalbe[87] of the relief gases shows that when blown off at 110° C. they contain no oxygen, indicating that all originally present in the digester has already been used up. He recommends relieving air when the temperature reaches 75° C. as the bisulfite is relatively stable at that temperature and the loss of gas will consequently be less. The presence of carbon dioxide and nitrogen in the relief gas in addition to the sulfur dioxide has been noted by several investigators. The amount of carbon dioxide formed is approximately 1.5 per cent of the pulp yield and is apparently a product of decomposition of the sugars formed during cooking.[85] The amount of nitrogen is approximately that present in the air in the digester. The relief at times also contains much liquor, and for this reason it is sometimes passed through a separator of some kind so that the gaseous portion may be conveyed to the liquor tanks to bring up the strength of the raw acid to the proper cooking strength. This recovery process is of the first importance in reducing the consumption of sulfur per ton of pulp. The total amount of sulfur dioxide relieved depends principally on the strength of the acid used and on the final blowing pressure in relation to the temperature at that stage. The amount of liquid relieved is governed largely by the amount of direct steam used and the moisture in the wood.

In practice the relieving of a digester is done from one or both of two points, through either the top or the side. It is claimed by Wimmer[115] that side relief is a help in systematic cooking and also aids in the recovery of gas and the reduction of sulfur per ton of pulp. To use the side relief to the best advantage he recommends relieving from the top for about 1½ to 2 hours, or until the temperature is 120° to 130° C. (248° to 266° F.), then, closing the top entirely, relieve
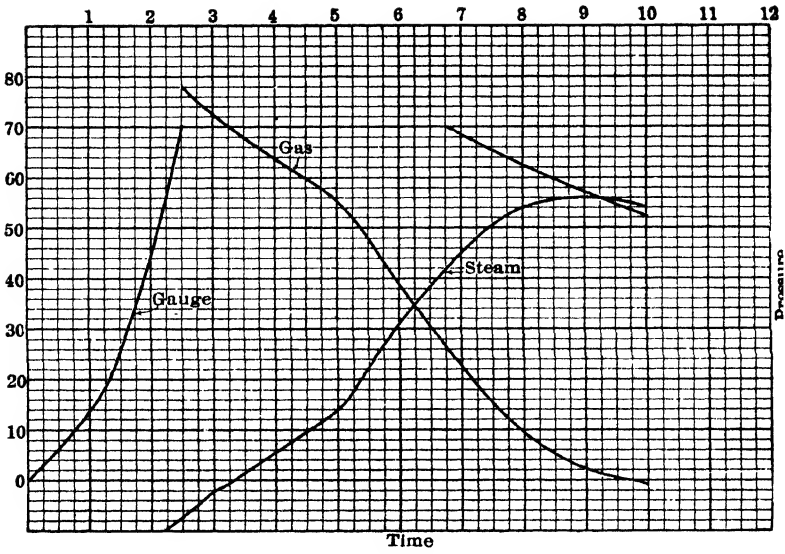
FIG. 29: SULFITE COOKING CHART.
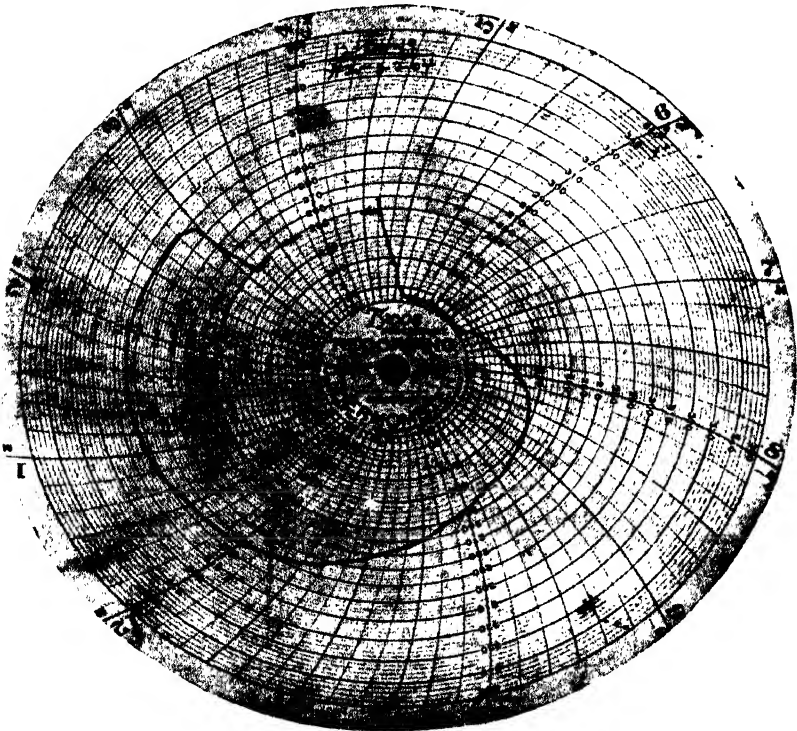
FIG. 30.   TEMPERATURE RECORD OF A SULFITE COOK.

(193)

from the side for $1\frac{1}{2}$ to 2 hours. After this, top relief can be started again and only dry gas will ordinarily be obtained to the end of the cook. On large digesters there should be from 3 to 5 hours of dry gas.

As already stated the composition of the acid liquor varies greatly in different mills. The many effects on yield and quality of pulp which may result indirectly from changes in the cooking acid composition are often confusing. It appears to be the general opinion among investigators that the sulfurous acid portion of the liquor influences principally the rate of penetration of the chips with the bisulfite, and the rate of cooking, an increase in concentration effecting more rapid rates in both instances. Since SO_2 is relieved from the digester during cooking the effects of initially strong acid are nullified to a considerable extent, except for the early part of the digestion. Higher operating pressures and lower temperatures enable the retention of greater amounts of SO_2 in the digester and thus enhance the effects of initially strong acid. Other results of sulfurous acid concentration which are more or less indirect, but often important, are improved circulation by the evolution of a greater quantity of gas and more uniform cooking of longer chips, both of which tend to improve the uniformity and cleanliness of the pulp. In some cases the strength of the pulp may also be affected indirectly. With a high concentration of SO_2 the temperature may be reduced to give the same cooking time used for lower concentrations. In such instances it is particularly important that the digester pressure be reduced before blowing to a point sufficient to maintain efficient recovery of SO_2.

The influence of increasing the concentration of combined SO_2 in the cooking liquor is mainly in the improvement of the yield and strength of the pulp. The effect is probably greater at concentrations less than 1.0 per cent than at higher concentrations. Concentrations less than 1.0 per cent are sometimes used commercially, but it is usually considered good practice to maintain at least 1.1 per cent and sometimes greater amounts.

Lowering the cooking temperatures tends to increase the time required for the same degree of purification but also tends to increase the yield and the uniformity of the pulp. The improvement in yield may be partly due to a decrease in screenings and also to slightly less destructive action on the cellulose. Miller and Swanson[65] concluded that the lowest average temperature which will give the required purification in the necessary length of cook will give the best pulp. They also found that the time of lignin removal was reduced approximately one-half by each 10° increase in temperature between 120° and 150° C. McGovern and Chidester[59] found an average reduction in

the yield of easy-bleaching pulp from western hemlock of 0.5 per cent for a 10° increase in the minimum temperature between 130° and 150° C.

In the cooking process irregularities are likely to occur from very obscure causes. Overcooking may be caused, according to Klason,[48] if too little lime is used. The minimum amount necessary to saturate the lignosulfonic acids is 22.5 grams per kilo of wood; with less than this amount the pulp is overcooked and charred. Overcooking may also result from decomposition of the liquor with formation of free sulfur according to the reaction

$$3SO_2 = 2SO_3 + S$$
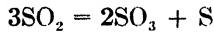
The sulfur acts catalytically, producing further decomposition of the calcium bisulfite, and the sulfuric acid combines with the lime as $CaSO_4$ so that not enough base is left to combine with the sulfonic acids, which polymerize, and eventually the fiber is attacked and darkened. Selenium in the cooking liquor produces similar but much greater effects than free sulfur.

The progress of a cook may be followed by various tests on liquor samples taken at intervals, or more directly by bleach tests on small samples of pulp blown from the digester. The different tests which may be used are described at the end of this chapter.

As an example of the rate of disappearance of SO_2 in a quick cook Genberg[29] gives the figures in Table 31.

TABLE 31

Cooking Time	SO_2	Cooking Time	SO_2
Hours	Per cent	Hours	Per cent
0	4.86	5	1.45
$\frac{1}{2}$	2.85	$5\frac{1}{4}$	1.27
$2\frac{1}{2}$	2.35	6	1.01
3	2.20	$6\frac{1}{2}$	0.78
$3\frac{1}{2}$	2.04	7	0.54
4	1.94	$7\frac{1}{2}$	0.22
$4\frac{1}{2}$	1.69	8	0.15

Recovery of Gas. The relief of gas and liquor from the digester removes a large quantity of sulfur dioxide, and its recovery is an important item in keeping the cost of sulfur used per ton of pulp at a low point. This is accomplished by passing the relief through separators and coolers from which the gas is taken to the acid-storage tanks where

it is absorbed and brings the acid to the desired strength for cooking. The liquid portion from the separator is either allowed to go to waste or the amount obtained up to a temperature of 130° to 135° C. is mixed with the acid from the acid system previous to strengthening the latter with relieved gas. The use of the portion of the liquid relief given off at higher temperatures is usually avoided owing to the danger of decomposition of the bisulfite. For cooking wet wood, particularly in warm weather, it is often desirable to avoid returning excessive quantities of the liquid relief to the acid make-up because of the difficulty in maintaining the strength of the acid. In the Chemipulp hot-acid process both gas and liquid relief are recovered in a pressure accumulator. In Thorne's[107] recovery system the separated and cooled gas from the digester is passed into the bottom of a tower filled with wood blocks over which the acid from the acid system is passed, the strengthened acid thus formed going to the storage tanks. The liquor from the separator contains about 1 per cent of SO_2, and after cooling it is sent to the acid system with the water or milk of lime as the case may be. This system is equally applicable to the limestone or milk-of-lime systems and by its use it is said to be possible to strengthen an acid of 2.60 per cent total and 1 per cent combined SO_2 up to 5.50 per cent total with no increase in the amount of combined; moreover, this is accomplished at a temperature of 35° C. (95° F.) with no loss of gas. Recovery towers of the Thorne type are now often used to absorb gas given off from the acid-storage tanks.

Some attempts have been made to recover the heat and gas liberated when the pulp is blown from the digesters into the blow pits. The results have not been very successful owing to the difficulties in handling the large volume of gas and steam given off in a very short time. However, a recent application of a spiral heat exchanger for this purpose is described by Rosenblad.[84]

The sulfur consumption is usually calculated as the weight of sulfur fed to the burners per ton of air-dry pulp produced. In commercial practice this figure may vary from about 200 pounds to more than 300 pounds depending mainly upon the efficiency of SO_2 recovery, the quality of pulp made, and the wood species used. The amount of sulfur actually consumed in the cooking process is usually considered to be approximately 175 pounds per ton of air-dry pulp.

Blowing and Washing. As already stated the contents of the digester are usually discharged into the blow pit under a pressure of about 50 pounds or less. The pipe from the digester to the blow pit may be of bronze or even cast iron. This pipe is so arranged that the stock is discharged against a target placed in one end of the blow pit,

to prevent wear on the pit walls. This target may be of bronze or of hard cast iron, which is generally used as it is cheaper and offers more resistance to mechanical wear than bronze. As the acid at this stage is comparatively weak and the blowing is immediately followed by washing the chemical resistance of the cast iron is sufficient for this purpose.

Blow pits are of various shapes but consist essentially of tanks with false bottoms through which the waste liquor may drain. The tanks may be constructed of the heartwood of southern pine or Douglas fir, or of concrete, lined with wood or tile. False bottoms constructed of tile with tapered perforations, widening toward the bottom, or more recently of perforated chrome-nickel stainless-steel plates, have largely replaced the perforated wood bottoms or cocoa matting formerly used. The water is introduced through a large supply line or sprinkler pipes at the top and drains off through the bottom. Several hours are required for the operation.

The treatment of the pulp after washing is largely a mechanical one, to remove dirt, knots, slivers, and uncooked or partly cooked chips, by means of rifflers, screens, etc. The screenings thus removed amount to 3 to 8 per cent of the pulp produced. During these mechanical purification processes the stock is very largely diluted; one authority gives the concentration of the stock as follows:

In rifflers .... 250 parts water to 1 part pulp
In coarse screens ...... 125 parts water to 1 part pulp
In fine screens .... 150 parts water to 1 part pulp

Pulp Qualities and Yields. The chemical composition of unbleached sulfite pulp depends upon the degree of delignification or amount of cooking, the species of wood, and to some extent upon variations in the wood of any one species. As the cooking proceeds up to the point of exhaustion of the bisulfite, reductions occur in the yield, in the lignin content of the pulp, and in its chlorine consumption or bleach requirement. At the same time the alpha-cellulose content of the pulp is increased and its viscosity in cuprammonium solution is lowered. When strong pulp is desired for use in the unbleached condition it is cooked less than for the more readily bleachable grades. In making pulp which is to be given further purification and bleaching treatment for the preparation of rayon and other cellulose derivatives, it is usually advantageous to accomplish as much purification as possible in the cooking treatment.

Tables 32 and 33 give some analyses of commercial unbleached sulfite pulps and also of experimental pulps prepared from a number of different species.

TABLE 32

YIELD AND CHEMICAL ANALYSES OF EXPERIMENTAL UNBLEACHED SULFITE PULPS FROM DIFFERENT SPECIES
(U. S. Forest Products Laboratory)

Species	Yield of Oven-Dry Pulp		Bleach Requirement (Bleach Powder with 35 Per Cent Available Chlorine)	Cellulose		Lignin	Total Pentosans	Ash	Solubility in			Viscosity (Cuprammonium Solution)
	Screened	Screenings		Total	Alpha				Alcohol-Benzene	Ether	1 Per Cent NaOH	
	Lb./100 lb. oven-dry wood		Lb./100 lb. oven-dry pulp	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Centipoises
White spruce	46.1 47.8	0.1 0.4	12 16	97.1 94.9	85.3 80.4	0.8 0.9	5.4 5.7	.. ..	1.3 1.2	0.6 0.7	.. ..	62.5 65.3
Norway spruce	47.2 49.3	0.5 0.8	6 15	97.9 94.4	85.1 79.6	0.8 0.6	4.6 5.5	0.4 0.5	1.9 1.5	1.2 1.0	10.2 12.7	83.5 97.0
Western hemlock	42.9 44.9	0.5 0.4	14 18	98.1 96.6	85.5 83.7	0.5 0.5	3.4 3.6	0.5 ..	0.6 2.1	0.9 0.2	.. ..	33.8 37.0
Eastern hemlock	43.5	0.4	18	95.5	83.1	1.5	4.0	0.6	0.7	0.2	..	
Lowland white fur	48.9 50.0	0.5 0.5	11 22	98.4 96.1	90.2 90.1	0.5 1.6	3.2 4.0	0.5 0.6	0.7 0.6	0.7 0.3	.. ..	
Silver fur	48.6 49.3	0.3 0.3	13 20	98.1 95.8	85.2 82.1	0.9 0.5	3.9 4.5	0.5 ..	0.6 0.4	0.2 0.6	.. ..	56.7 73.1
Loblolly pine	46.6 48.1	1.5 1.8	14 21	98.2 95.9	86.7 82.6	0.4 0.4	4.7 6.1	0.4 ..	1.7 1.2	0.7 1.0	.. ..	38.1 76.5
Aspen White birch Black gum	49.4 45.0 47.3	1.1 1.0 0.9	8 8 10	98.3 96.6 98.4	88.2 84.0 90.0	0.8 2.0 0.6	6.5 5.9 5.9	.. .. ..	1.03 1.8 1.3	1.2 0.7 0.5	12.4 12.0 10.7	.. .. ..

TABLE 33

CHEMICAL ANALYSES OF COMMERCIAL UNBLEACHED SULFITE PULPS

(U. S. Forest Products Laboratory)

| Species | Cellulose | | Lignin | Total Pentosans | Solubility in | | | | Ash | Viscosity (Cuprammonium Solution) |
| | Total | Alpha | | | Alcohol-Benzene | Ether | 1 Per Cent NaOH | Hot Water | | |
	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Centipoises
Spruce	95.7	81.2	1.0	5.1	1.5	0.9	10.3	....	0.4	30.4
80% spruce 20% Balsam	97.2	85.4	0.8	5.2	1.0	0.5	....	....	0.35	74.8
Spruce	94.6	82.2	....	....	....	....	11.4	1.2	....	....
	97.0	84.9	2.2	....	....	....	13.1	1.3	....	....
	96.6	86.3	1.2	....	....	....	11.8	0.2	....	....
Hemlock	95.0	72.7	3.5	....	....	....	9.9	1.0	....	....
	92.4	83.8	1.4	....	....	....	14.2	0.5	....	....
	98.3	78.6	0.8	....	....	....	12.7	nil	....	....
	95.8	79.9	2.7	....	....	....	12.7	0.2	....	....
Norway spruce	94.6	80.7	0.8	5.8	1.4	0.8	9.4	....	0.5	137.0

Certain species, the firs, aspen, and black gum, show relatively high alpha-cellulose values for a given degree of cooking, no doubt a result of relatively large amounts present originally in the wood. This characteristic is also usually reflected in a high pulp yield on a weight basis. Other reflections of the original composition of the wood are the higher pentosan contents of the hardwood pulps and the high ether solubility of the pulps from the more resinous woods.

Table 34 gives various constituents of western hemlock and their removal during sulfite cooking. The removal of nearly all the lignin and a large portion of the pentosans is particularly characteristic of the acid sulfite treatment. At the same time a considerable quantity of the total cellulose and some of the alpha-cellulose go into solution.

TABLE 34

COMPOSITION OF WESTERN HEMLOCK, CONSTITUENTS REMOVED DURING COOKING
BY THE SULFITE PROCESS, AND COMPOSITION OF SULFITE PULP
(U. S. Forest Products Laboratory)

	Composition of Wood	Constituents Removed during Cooking	Constituents Remaining in the Pulp	Composition of Pulp
	Per cent	Per cent (based on the original wood)		Per cent
Cellulose				
Total............	59.8	17.7	42.1	98.1
Alpha............	42.6	5.9	36.7	85.5
Lignin.............	29.1	28.9	0.2	0.5
Pentosans.........	9.6	8.1	1.5	3.4
Material soluble in				
Alcohol-benzene....	2.2	1.9	0.3	0.7
Ether............	0.5	0.4	0.1	0.2
Hot water.........	3.1	...	...	...
Ash...............	0.3	0.1	0.2	0.5

Yield of screened pulp — 42.9 pounds oven-dry pulp per 100 pounds oven-dry wood.
Chlorine consumption of pulp — 3.35 per cent.

It is often observed that unbleached sulfite develops a reddish color when stored in the wet condition and exposed to light and air. Heuser and Samuelsen[33] express the opinion that the unknown substances in the wood which cause the red coloration in pulp are largely dissolved during the sulfite cook, but that small portions of tannins or lignin, or their decomposition products, remain and are influential in causing this trouble. Hägglund and Hedman[34] found that the red color was connected with the solid lignosulfonic acid present in the pulp. They

thought that the color could be traced to an oxidation whereby a quinoid rearrangement in the lignin molecule occurred. This oxidation was shown to be accelerated by small amounts of copper.

The ash in sulfite spruce fiber has been given considerable study by Richter,[80] who finds that it rarely exceeds 1 per cent and is usually about 0.5 per cent. Silica, generally amounting to about one-third of the total ash, is probably fixed as calcium or magnesium silicate during cooking, as the silica present in the wood is too little to account for so much in the fiber ash. The percentage of iron in the ash showed no constant relationship to the total ash or to any characteristics of the pulp.

The resin in sulfite has been given much attention because of its possible relation to pitch spots in the paper and serious operating difficulties.

Amounts of extractives have been reported for different types of sulfite pulp as in Table 35.

TABLE 35

	Ether Soluble	Alcohol Soluble	Total
	Per cent	Per cent	Per cent
Foreign sulfites[81]................	0.70–1.33	0.10–0.22	0.90–1.43
American sulfites[81]	0.65–1.21	0.15–0.62	0.86–1.52
Unbleached fiber[88]..............	0.82–0.98	0.18–0.82	1.05–1.67
Bleached fiber[88]	0.66–0.98	0.23–0.62	1.00–1.60

In general, the ether-soluble portion of the pulp is considered to be the principal cause of troubles with pitch. A value of 1.0 per cent is often considered the maximum above which difficulties may occur. Pitch contains fatty and resinous constituents and, in addition, inert unsaponifiable material. According to Sieber,[92] the cooking liquor removed in one instance only 4.2 per cent of the wood resins; 51.8 per cent was removed in the washing operations, and 15 per cent during the bleaching. He found pitch deposits in paper to be similar to the ether-soluble portions of the wood resins. However, the ether extract alone is not a fully reliable criterion. Rägan and Kress,[77] believing the tackiness of the pitch to be the cause of the difficulties, developed a test to determine this factor.

Seasoning the wood is probably the most common method of avoiding pitch trouble. The resin soluble in ether and alcohol is reduced by this method. Changes in the character of the resin extracted from the wood indicate that storage of chips for 2 or 3 weeks in the open air

is as effective as storing the logs for 2 years.   Richter[82] gives the figures in Table 36 for resin in pulp from the same wood, wet and dry.

TABLE 36

Moisture in Wood	Resin in Cellulose		
	Ether Soluble	Alcohol Soluble	Total
Per cent	Per cent	Per cent	Per cent
49.0	1.00	0 11	1.11
0.5	0.38	0.26	0.64
35 0	1.31	0.31	1.62
5.0	0.88	0.36	1.24

Enckell[24] considers the colloidal aspects of pitch behavior and suggests remedies of three types: (a) stabilizing the resin suspension by the addition of such materials as gelatin or starch; (b) absorption of the resin particles on china clay, bentonite, or talc to prevent their agglomeration; and (c) fixation on the fibers by the addition of aluminum sulfate and an alkali.   Favorable results from the addition of waste sulfite liquor and alum in proper proportions to the slush stock are reported by Brauns.[13]   Separation of the fine fiber fraction, including the ray cells in which a large portion of the resin is concentrated, by screening, is sometimes practiced in both Europe and America.   Edge[22] reports that a removal of 2 per cent of the pulp in this manner takes out 20 to 50 per cent of the pitch and most of the dirt and ash constituents.   Carpenter[17] reports a reduction in ether-soluble material in pulp from southern pines from more than 1 per cent to 0.6 per cent by a somewhat similar method.   Fritz[27] proposes treatment of the pulp with a solvent such as kerosene and emulsifying the solution with an emulsifying agent.   Many other methods, including the adjustment of the temperature and acidity of the stock, use of soft water, elimination of excessive admixture of the stock with air, washing the pulp with hot water containing soda ash, and addition of sodium thiosulfate, alum, or diatomaceous silica, have been suggested.   Difficulties are very often governed by local conditions and therefore may require different treatments.

Bleaching largely eliminates resin troubles, and with well-bleached pulp trouble from this source is seldom encountered.

For the demonstration of resin in sulfite fiber, Klemm[52] uses a strong solution of Sudan III in a mixture of 3 parts alcohol and 1 part water. The sample is reduced to a pulp with water, drained, and the moist fibers treated with the dye.   The excess is removed by blotting paper and the fibers mounted for observation in water.   The resin will be

found stained orange-red while the fiber is uncolored. Noll and Hahn[71] report improved results with new Sudan dyes, Sudan Orange RR, Sudan Red 5B, and Sudan Black B. The last is the most visible in both daylight and artificial light.

Modifications of the Quick-Cook Process. During recent years important advances have been made in the methods of cooking to improve the uniformity and control of cooking conditions and in the recovery of heat and SO_2.

Heat from the digester relief is recovered in the Decker[21] process by passing the relief from digesters being relieved into the bottom of one being started, in place of steam. This operation is continued until the next digester is ready to be started. The relief is then passed into the next digester and the first cook completed with steam.

The Chemipulp hot-acid recovery system affords a means of recovering heat from the digester relief while also obtaining more favorable and uniform conditions, particularly during the early part of a digestion, than are realized under the procedure customary with cold acid. The method consists essentially in passing the hot relief liquors from the digester into a pressure accumulator (usually a spherical tank) having a capacity of one and one-third or more charges of cooking acid. The accumulator is lined with materials used for the digester lining. Where extra digester space is available digesters have been operated as accumulators. In the accumulator the relief gas and liquid are mixed with cold acid pumped from the storage tank, preferably connected to give a continuous supply. The gases not absorbed in the accumulator are conducted to the absorption tank. The resulting hot liquor charge is pumped from the accumulator into the digesters at a temperature of 70° to 75° C. after the digester has been filled with chips. With the digester cover bolted on the pumping may continue to develop a hydrostatic pressure of about 40 pounds per square inch. The relief valves may then be opened and the liquor circulated through the digester and accumulator for periods up to 2 to 3 hours to improve uniformity and maintain the strength of the acid. Steam consumption is thus decreased and wide variations in temperature which would occur with rapid introduction of steam during this period are avoided.

To maintain uniformity of temperature in the digester, thus obtaining a close control over the cooking operation, and at the same time to avoid dilution of the liquor with steam, methods of forced liquor circulation and indirect heating have been adopted. In 1913 Morterud[68] proposed to pump the liquor from the bottom of the digester through a heater and back into the top. Although forced liquor circulation and indirect heating have been widely used in cooking sulfate pulp, until

the chrome-nickel steels were developed they were not applied very extensively to the sulfite process owing to the difficulty in finding suitable materials for constructing the heaters. The liquor may be circulated in a number of ways. It may be pumped from the top of the digester and back into the bottom; from the side into both top and bottom; or, as proposed by Morterud, from the bottom and back into the top.

The development of a modern method is well described by Swanson, Lang, and Smith.[101] Numerous temperature measurements made at different points in a digester showed variations of as much as 100° C. in the early part of a direct cook with natural circulation. After installation of a heater and forced circulating system and establishing a suitable rate of circulating the liquor, the differences in temperature were reduced to as little as 10° during the heating period. However, the maximum uniformity was attained by the additional use of a mechanical chip distributor, which eliminated some channeling and materially increased the amount of chips charged. The more positive control of cooking conditions permitted the use of automatic temperature and pressure regulators and the so-called time-cycle control whereby the temperature and pressure are regulated automatically by means of cams cut to follow the desired curves. Location of the temperature-sensitive element in the liquor leaving the heater gives an almost immediate response in the controller to temperature changes. The installation resulted in a uniform cooking time for all cooks, improvement in the strength of the pulp for the same degree of cooking, improvement in the yield of pulp from a unit of wood, an additional increase in the yield per digester, and consequent reduction in the chemicals consumed. The steam consumption was decreased about 10 per cent, and an additional advantage was obtained by returning the condensate from the heater to the boiler plant.

To prevent the formation of excessive scale in indirect heaters applied to circulating systems, it is apparently desirable to maintain a liquor velocity in the heater tubes of at least above 8 feet per second. Also, a sufficient amount of SO_2 should be carried in the acid to prevent precipitation of $CaSO_3$ in the heater tubes. Perhaps of equal importance the $CaSO_4$ should be kept low, also to avoid precipitation.

In some instances liquor-circulating systems are used without heaters, and various combinations of hot acid, forced circulation, and indirect heating have been adopted.

By-Products and Waste Liquor. The sulfite process offers opportunities for the recovery of by-products which are now lost during the period of relieving or in the waste liquor. Bergström[8] states that the

vapors condensed from the digesters yield an aqueous distillate containing methyl alcohol, acetone, aldehyde, and traces of acetic and formic acids together with a brown oil floating on the surface. This oil contains 7 per cent boiling between 150° and 160° C., 55 per cent boiling from 160° to 190° C., and 17 per cent boiling between 190° and 210° C. The portion boiling between 160° and 190° C. consists largely of cymene. The specific gravity of the various fractions varies from 0.845 to 0.951. Many efforts have been made to utilize this cymene, or " sulfite turpentine," but they have not met with any very great success. Certain classes of dyes and intermediates have been made from it, and it has been shown to have considerable value as a thinner for paint and varnish. The manufacture of perfume is said to be one of the principal uses of cymene at the present time. Crude cymene amounting to 0.36 to 1.0 gallon per ton of pulp may be obtained by passing the digester relief through a condenser, or by skimming it from the surface of the acid in the storage tanks. The crude cymene, containing 75 to 85 per cent p-cymene, may be purified by removing the SO_2 and by distillation. Methods for recovering and purifying the crude cymene are described by Obermanns,[72] Nickerson,[70] and Groggins.[31]

Bergström[9] also claims that in the Ritter-Kellner process 8 to 10 kg. of methyl alcohol are formed per ton of easy-bleaching cellulose produced; of this about 3 kg. may be obtained from the relieved gases. If the waste lyes are distilled in a continuous-column apparatus the distillate contains methyl alcohol, acetaldehyde, acetone, oils, and SO_2 as well as small quantities of formic and acetic acids.

The problem presented by the waste liquors of the sulfite process is one which not only is interesting from a chemical standpoint but also has attracted much attention because of its bearing on stream pollution. Some mills have either been obliged to close or to find suitable methods of reducing the pollution. A great amount of investigative work toward a solution of the problem is under way, and it appears to be only a question of time before satisfactory methods are found. When such methods are available legislative demands for more complete purification will undoubtedly be made.

Waste sulfite liquor contains the soluble products of digestion amounting to 50 per cent or more of the original wood substance. Therefore for every ton of pulp produced about 1 ton of dissolved material is wasted. The total amount of dissolved solids in the waste liquor produced in the United States in 1937 was about 2,000,000 tons. Probably the most important pollutional effect results from its depletion of the dissolved oxygen of the water. It is estimated that for 1 ton of

pulp this pollutional effect is equivalent to the daily domestic sewage from 1500 persons.[112] Though the possibilities of obtaining valuable by-products from this huge waste are still attractive and are closely related to the problem of disposal, the disposal itself is of primary urgency.

A number of methods for eliminating or reducing pollution by waste sulfite liquor have been tried with varying degrees of success. Aeration of the liquor has in some cases reduced the biochemical oxygen demand to a more satisfactory figure. Storage of the liquor in artificial basins, depending upon solar evaporation, is seldom practicable and has incurred difficulties arising from underground seepage. Neutralizing the liquor with lime lowers its acidity but does not materially reduce its pollutional characteristics. None of these methods has been very widely used, and they provide no means of realizing any value from the liquor.

Evaporation of the liquor to give for some purposes a more concentrated solution, and for others a solid material, has been practiced to a limited extent for a number of years. When all the liquor is handled in this manner its discharge as waste is practically eliminated. It provides a means of utilizing its fuel value and of obtaining a number of useful products. The principal objection to evaporation is the cost of handling the large quantity of water, amounting to 85 to 90 per cent of the concentrated liquor before dilution with wash water. Evaporators may be constructed of iron or steel when the liquor is first neutralized; otherwise copper, bronze, or preferably stainless steel is necessary.

Less than half of the liquor discharged from the digesters will drain from the pulp in the blow pits without dilution with wash water. Of a total quantity of about 2400 gallons per ton of pulp, according to Johnsen[44] only 740 to 800 gallons can be obtained in this manner without special equipment. Use of screw presses or vacuum washers for washing the pulp makes possible a recovery of 95 per cent or more of the solids dissolved in the liquor without further dilution.

Both acid and alkaline precipitation methods have been proposed for removing the solids from the liquor. Strehlenert[97] adds acid sodium sulfate to the fresh, hot liquor to precipitate calcium sulfate. The liquor is then heated under pressure to a temperature of 200° C. Sulfur dioxide is recovered and the lignin precipitated and used as fuel.

Howard[40] uses a fractional precipitation accomplished by the addition of calcium hydroxide. The precipitate obtained in the first step consists mainly of calcium sulfite which is employed in making the

cooking liquor. The precipitate obtained in the second step contains the organic lignin material and is used for the recovery of by-products and as fuel. The effluent, after a final stripping treatment, contains principally the carbohydrate material. The oxygen demand of the effluent is thereby considerably reduced from that of the original waste liquor. Vanillin, tanning material, and other materials for making plastics are recovered as by-products. The commercial feasibility of the method is indicated by its operation in a Wisconsin mill on a full-plant scale. Operating profit, exclusive of any return from by-products, depends largely upon the fuel costs, which can be eliminated in particular instances.

Considerations of waste-liquor recovery have included the feasibility of using more expensive soluble bases such as sodium, ammonia, or magnesium, which might be made possible by the development of suitable methods of recovery. Certain advantages resulting from their use, particularly in pulping resinous woods, have already been pointed out. Numerous methods including those of Drewsen, Bradley and McKeefe, Richter, and the U. S. Forest Products Laboratory have been proposed for recovering soda from sodium bisulfite or neutral sulfite liquor. The recovery of soda is somewhat simplified in a sulfite mill operating in conjunction with a kraft mill where the waste liquor can be handled along with kraft black liquor. The method proposed by the Forest Products Laboratory[12] for recovering soda-base liquor, which could be used independently, consists in evaporation and burning the liquor in a manner similar to that for kraft liquor recovery. The resulting smelt is largely composed of sodium carbonate and sodium sulfide. Heating with moist sodium bicarbonate converts the sodium sulfide to carbonate with the evolution of hydrogen sulfide, which can be burned to sulfur dioxide and used for making the cooking acid. The sodium bicarbonate is obtained from part of the sodium carbonate by passing carbon dioxide into a sodium carbonate solution. The remainder of the carbonate is then converted to sodium sulfite or bisulfite by introduction of sulfur dioxide. The carbon dioxide evolved is utilized in the preparation of the sodium bicarbonate. This method of converting the sodium sulfide thus avoids the formation of thiosulfate and polythionates which are detrimental to the cooking process. Soda-base liquors are used commercially to a limited extent in the United States and in Europe.

Ammonia can be recovered from ammonium bisulfite liquor by making it alkaline and distilling with steam, or bubbling air through the hot liquor.[79] It appears questionable whether the cost of using ammonia-base liquor together with recovery of ammonia by these

methods would be as low as that for other bases, and the disposal of the alkaline liquor residue still remains a problem.

The relative ease with which magnesium can be recovered from magnesium bisulfite liquor by methods of evaporation and burning, owing to the fact that the liquor burns readily to form magnesium oxide and a considerable quantity of sulfur dioxide, offers interesting possibilities in spite of the relatively high cost of the make-up chemical. The magnesium oxide can be converted directly to the bisulfite by contact with sulfur dioxide. Efficient methods of chemical recovery and utilization of the fuel value of the liquor to generate steam would apparently effect an economic disposal of the waste liquor.[109]

The exact composition of waste sulfite liquor is not as yet known completely. It contains sugars resulting from hydrolysis of hemicelluloses and the combination of calcium with sulfonated lignin which may be considered as the calcium salt of lignosulfonic acid. The structure of the latter as well as the structure of lignin itself is still the subject of a large amount of investigative work.

Bryant[14] gives the following composition of waste liquor obtained in cooking hemlock:

	GRAMS PER LITER	POUNDS PER TON OF PULP
Total solids	115.00	2999
Loss on ignition	105.36	2748
Ash	9.64	251
Total sulfur	7.83	204
Sulfur as SO_3	0.76	20

The specific gravity of this liquor was 1.0425.

From the answers given by 18 mills to a questionnaire sent out by Genberg the total solids on evaporation, ash in total solids, and heating value of the solids are found to be as follows:

	MAXIMUM	MINIMUM	AVERAGE
Total solids, per cent	12.39	9.50	11.0
Ash in solids, per cent	15.4	5.00	10.4
Heating value, B.t.u. per pound....	8990.0	6942.0	7859.0

Klason[50] calculates that for every ton (2202 pounds) of dry fiber produced the waste liquor contains the following:

    600 kg. (1320 pounds) lignin.
    200 kg. (441 pounds) sulfur dioxide combined with lignin.
     90 kg. (198 pounds) CaO combined with lignosulfonic acid.
    325 kg. (717 pounds) carbohydrates.
     15 kg. (33 pounds) proteins.
     30 kg. (66 pounds) resin and fat.

According to Krause,[56] the principal constituent in the waste liquor is the calcium salt of lignosulfonic acid. Ritter-Kellner liquor is darker and contains more furfural and generally more sugars than Mitscherlich liquor. Wood boiled in the autumn contains about twice as much sugar as wood obtained in the spring. Very careful analyses of liquor from autumn-cut wood gave the figures in Table 37.

TABLE 37

	Mitscherlich Process	Ritter-Kellner Process
	Per cent	Per cent
Furfural	0.01	0.02
Pentosans	0.40	0.29
Hexosans	0.21	0.49
Total sugars	1.48	1.47
Pentoses	0.47	0.41
Mannose	0.48	0.48
Levulose	0.28	0.25
Galactose	0.01	0.01
Dextrose	....	Trace

The hydrolysis of carbohydrates into sugars during sulfite cooking occurs mostly above 100° C., as pointed out by Sherrard and Suhm,[91] and roughly parallels the lignin removal. The sugars formed may amount to as much as 15 to 20 per cent of the weight of the wood, depending upon the temperature schedule and to some extent upon the acid composition.[33]

Hoenig[39] claims that no organic acids except formic and acetic are present and that the ratio of these is 1 : 1.56. He finds 2.15 to 9.08 grams of volatile acid per liter.

The waste liquor, according to Walker,[111] yields brominated and chlorinated products; it contains active carbonyl and methyl groups and is a strong reducing agent. On addition of alcohol the chief constituents are precipitated as a dark, gummy mass which becomes brittle on drying. This may also be obtained by salting out with sodium chloride or by treating with concentrated mineral acids or lead acetate. It is almost impossible to purify this substance because of its colloidal nature and its limited solubility in the usual organic solvents.

The attempts to utilize the materials in this waste liquor have been very numerous, and many patents have been issued covering all kinds of applications. A complete enumeration of all the patents in detail would occupy too much space; moreover, they have been well covered

by Müller[60] up to the year 1911, by Johnsen and Hovey,[45] and by West.[113] A brief outline of the more important uses, or proposed uses, is therefore all that will be attempted here.

A limited utilization of the liquor is obtained in a number of commercial products prepared from evaporated liquor. These consist mainly of binders or adhesives, tanning material, and, in a few instances, fuel.

Use of waste sulfite liquor as a road binder has increased materially in Sweden and in the United States. Benson[6] describes three methods of application practiced in Sweden. The first consists of sprinkling with concentrated liquor diluted with 2 parts of water, 1 kg. of concentrated liquor being applied per square meter of roadway. In the second method, lime (1 to 2 per cent of the solids in the liquor) is applied after the sprinkling, to precipitate a certain amount of the solids. In the third method a hygroscopic salt such as calcium chloride is applied after the liquor treatment. This treatment is thought to improve the plastic properties of the road and improve its wearing qualities. In the United States considerable quantities of the concentrated liquor known as Raylig and lignin binder are used on roads in Oregon and Washington, and also in New Jersey and Maryland. According to Westlund,[114] the material can be applied cold with water sprinklers. It penetrates deeply and sets up quickly to give a hard, smooth, dustless surface, which can be opened to traffic 2 to 6 hours after application. The surface is not permanent but requires occasional blading and sprinkling. Costs vary from $180 to $300 per mile, depending upon the transportation necessary and quantities purchased.

Use of the concentrated liquor in preparing briquettes from waste coal has met with some success, the briquettes being hard and making excellent fuel in ordinary grates or in smelting furnaces. An advantage which it possesses for this work is that the briquettes do not soften on heating and hence hold their shape well in use. On the other hand, the high percentages of ash and sulfur are detrimental in some cases. The briquetting of pyrites, wood waste, iron ores, and other materials has also been successfully carried out by means of the concentrated waste liquor. Another use as a binder is in the iron foundry where it is mixed with the sand in preparing the molds. Stutzer[98] gives the following as the composition of a sulfite waste liquor and two concentrated products made therefrom:

	ORIGINAL WASTE LIQUOR	WOOD EXTRACT	CELL PITCH
Dry matter	12.18	63.88	82.79
Ash constituents	1.44	2.64	14.90
Lime	0.87	0.50	8.50
Total sulfur	0.85	4.80	5.87
SO₂	0.24	0.15	0.85

The adhesive properties of the liquor are found particularly desirable for cementing linoleum to floors. For this purpose the concentrated liquor is mixed with a clay base and a preservative.

The preparation of a material for making insulating substances or artificial leather is patented by Trainer.[110] The waste liquor is evaporated to 30° Bé. and then heated with an acid, preferably after adding an aldehyde such as formaldehyde.

Extracts for use in tanning leather are prepared in considerable quantities by processes involving neutralization with lime, concentration, and subsequent separation of the organic and inorganic materials. The extracts obtained contain practically no true tannins but do contain materials which are taken up by the skins and act as fillers. Though these extracts are not suitable for tanning alone they find a legitimate use as additions to other true tanning substances.

Utilization of waste sulfite liquor as fuel offers perhaps one of the simplest means of disposal. This use in connection with the Howard precipitation process has been mentioned, and the heat value of the solids in the liquor has been stated. Analyses and heat balance calculations for methods for burning concentrated liquor made by Kimball[47] show the results to be expected from these procedures. In most cases burning the liquor should furnish sufficient steam for evaporation of the liquor and for other mill requirements.

The preparation of alcohol[105,36,46,89] from waste liquor has probably attracted more attention than any other method of utilization, and a number of commercial plants are in successful operation in Europe. The two principal processes now in use are the Swedish, which is a combination of the Wallin and Ekström processes, and the Norwegian or Landmark method. The principle of all processes is the fermentation of the sugars present followed by the distillation of the alcohol formed, and one of the principal difficulties encountered has been due to the poisoning of the yeast by traces of sulfur dioxide. The Swedish process uses a tempered yeast which is capable of resisting this action. The liquor is first neutralized by calcium carbonate and the last traces of acidity by calcium hydroxide; it is then cooled, settled, and run to the fermentation vats where the yeast is added. It is fermented at

27° C. for 4 or 5 days and then distilled. The raw alcohol contains 92 to 93 per cent of ethyl alcohol, 3 to 4 per cent methyl alcohol, and small amounts of cymol, acetone, and aldehyde. The yield of 100 per cent alcohol by this process is said to be 74 liters per ton of dry sulfite, and the cost about 12 cents per U. S. gallon 180 proof.

In the Norwegian process the fermentation is aided by a nutrient and easily fermentable medium prepared from milk or whey. To the milk an equal volume of sulfite liquor is added and a small amount of muriatic acid, and the precipitated lignocasein filtered off. The filtrate is then added to the waste liquor and the mixture evaporated to a concentration of about 15 per cent. It is next neutralized by powdered limestone, cooled to 27° C., and the yeast added; in this process ordinary brewers' yeast has proved entirely satisfactory. After 4 or 5 days' fermentation it is ready to be distilled. The yield by this process is claimed to be 91.2 liters of 100 per cent alcohol per ton of dry sulfite, and the cost about 9 cents per U. S. gallon 180 proof.

According to McKee,[60] the so-called poisoning of the yeast is not due to sulfur dioxide but to the lack of oxygen. He has patented a process in which the hot waste liquor is cooled by blowing air through it and then placed in closed fermentation tanks where it is kept agitated during the fermentation period by a slow current of air. Under these conditions fermentation proceeds satisfactorily with ordinary yeast even in the presence of very considerable amounts of sulfur dioxide. Loss of alcohol is prevented by scrubbing the exit gases from the fermentation tanks with unfermented liquor.

According to the United States Bureau of Foreign and Domestic Commerce figures reported by Benson,[6] the production of alcohol from waste sulfite liquor in Sweden amounted to 15,782,000 liters in 1930. The total annual capacity for the same year was 20,000,000 liters.

Even though the preparation of alcohol from the waste liquor may be a profitable undertaking it does not solve the problem of the disposal of the liquor since the spent fermentation residues are nearly as objectionable as the original waste. The production of alcohol should therefore be considered only as a possible by-product step in a more comprehensive disposal scheme. McKee[61] proposes to use these as a fuel after concentrating to 50 per cent solids.

In a method used in a Canadian mill[4] for making bakers' yeast from waste sulfite liquor, lime or soda is added to the liquor to give a pH value of 6.0 to 6.5. After settling for 24 hours the liquid is decanted, cooled to 28 to 30° C., and filtered. Molasses to give a sugar content of 3 to 5 per cent, yeast, malt, acid ammonium sulfate, and superphosphate are then added, and air is supplied to the solution. The

yeast is separated, washed, and filtered. From the liquor from 1 ton of pulp, 350 to 450 pounds of yeast are obtained. The capacity of the plant is 20,000 pounds of yeast per week. Fodder yeast containing 53 per cent proteins has been prepared by Fink.[25]

Stutzer[99] has investigated the possibilities of waste liquor in the preparation of cattle feed; he asserts that in each kilo, containing 120 grams per liter of solids, there are 550 calories which can be made available by feeding. His proposed treatment is to evaporate 100 liters to 50 liters in a vacuum, mix with 0.5 kg. of formaldehyde and ground limestone, and then filter. The filtrate, after further evaporation, is mixed with molasses and 6.25 kg. of peat to give 45 kg. of cattle food.

Various agricultural uses of waste sulfite liquor have been suggested. It has been proposed by Knösel[53] to prepare a fertilizer from the waste liquor by evaporating to about 25° Bé. and mixing with about an equal weight of ground Thomas slag. Analyses of this product show that practically all the phosphoric acid is in the citrate-soluble form. Tests of ammoniated sulfite liquor described by Phillips[76] and others indicated that though the sulfite liquor thus treated might have value as a potential source of nitrogen, as a soil conditioner, or as a source of humus, it was less effective as an intermediate nitrogen source than either dried blood or a mixture of sodium nitrate and ammonium sulfate. A successful method of using waste sulfite liquor for a fertilizer should provide an outlet for large quantities.

Sulfite waste liquor in concentrated form has been found by Hurt[41] to be a very suitable emulsifying agent for agricultural sprays. Fleming and Reedy[26] prepared a lime-sulfur spray material by passing hydrogen sulfide into the liquor to form calcium sulfide and sulfur from the bisulfite present.

The production of vanillin from waste sulfite liquor, already mentioned in connection with the Howard process, has recently become of commercial importance in the United States and Canada. In general, the methods of preparation consist in treating the liquor or lignin complex precipitated from it with hot caustic solution. The vanillin is separated either by steam distillation or by extraction with one of the higher alcohols or benzol, and distilled. The limited market for vanillin in comparison with the volume that could be supplied is indicated by the fact that the present requirements of the United States could be easily supplied by one or two mills. On the other hand, vanillin appears to have potential value for dye intermediates and other purposes which would lead to a wider use if the price can be reduced sufficiently.

The use of sulfite waste liquor in the sizing of paper has been pro-posed by Mitscherlich,[67] who mixed the liquor with gelatin solution and separated the precipitate formed. This was then dissolved in weak alkali and added to the paper stock in which it was precipitated by alum. A sizing process of another kind is that of Klason,[49] in which the waste liquor is used instead of alum as a precipitant for silicate of soda. Neither of these processes has ever come into extensive use.

In the dyestuff industry it has been used as the basis for the manu-facture of sulfur dyes, in the reduction of indigo, and in the preparation of indanthrene and similar dyes. The sodium lignin sulfonate pre-pared from it has been employed to replace tartaric acid in mordanting wool.

Other substances which it has been proposed to recover from the waste liquor are antiseptic materials, calcium sulfite, calcium sulfate, coniferin, cymol, acetic acid, furfural, levulinic acid, oxalic acid, sulfur, turpentine, lignoresin, etc. Many of these can be obtained only in small amounts, and the demand and the prices obtainable are not such as to make the undertaking attractive.

Although much progress has been made there is still much to be done before the utilization of this enormous amount of waste can be con-sidered satisfactory. The quantity of material to be handled would seem to indicate that such investigations should be directed towards the production of large amounts of products at small profits rather than the preparation of small quantities of substances of relatively high value per pound.

Tests and Analyses for the Sulfite Process. *Sulfur.* The sulfur at present on the American market is of very high purity and usually needs only an occasional examination. A good sulfur should contain less than 1 per cent of foreign matter.

Moisture may be determined by drying a 3- to 5-gram portion to constant weight at 70° to 80° C. The heating should not be un-necessarily prolonged nor should the temperature be allowed to rise too high.

To determine non-volatile substances a 10-gram sample is cautiously heated in a porcelain crucible on a sand bath until nearly all the sulfur has volatilized (ignition of the sulfur must not take place). Cover the crucible with a perforated lid and pass into it pure, dry hydrogen gas until all sulfur has escaped; cool and weigh as non-volatile matter.

Inorganic ash may be determined by igniting the non-volatile matter with access of air and reweighing after cooling.

The sulfur itself can be determined[102] by extracting a 1-gram sample with carbon bisulfide for 15 minutes on a Gooch crucible or a Jena-glass

extraction thimble. The residue is dried and weighed, and the percentage of sulfur is the difference between 100 per cent and the percentage of insoluble material.

For determining selenium in sulfur[102] mix a 10-gram sample with 50 grams of a flux consisting of 4 parts sodium carbonate and 1 part sodium nitrate, and heat to fusion in a nickel crucible. Extract the melt with water, acidify the solution with hydrochloric acid, and boil to remove chlorine. Mix the solution with an equal volume of concentrated hydrochloric acid, and saturate with SO_2 to precipitate metallic selenium. Filter through a Gooch crucible with previously dried and weighed asbestos mat and wash the precipitate with concentrated hydrochloric acid, dilute hydrochloric acid, water free from acid, and lastly with alcohol. Dry the residue at 105° C., and weigh as metallic selenium.

Another method for determining selenium is described by Smith.[95]

Burner Gases. In order to control the burners properly the gases should be tested once an hour, or oftener if the burners are not working satisfactorily. The sulfur dioxide may be determined by means of an Orsat apparatus using caustic soda or a 50 per cent solution of chromic acid in water in the absorption pipette. The gas is measured in the burette over mercury or water, which soon becomes saturated with SO_2 and then introduces only a very slight error.

Several instruments are available for measuring and recording the SO_2 in the burner gas. The Superior recorder mixes constant volumes of gas and water, automatically measures the conductivity of the solution, and records the result as percentage on a chart. The Leeds-Northrup recorder operates on the electric-resistance principle, measuring the resistance of the burner gas in a gas-analysis cell and registering on a calibrated chart the resistance changes in the cell by means of a potentiometer recorder.

Excess air may be estimated by determining the oxygen by means of alkaline pyrogallate after first absorbing the SO_2 in caustic soda. This test gives valuable information regarding leaks in the apparatus between the combustion chamber and the absorption system.

Sulfur trioxide in the gases is very difficult to determine with accuracy. Richter[83] passes the gas, at a rate of 1000 cc. in 20 to 25 minutes, first through a hard-glass sampling tube surrounded with an iron jacket and then through a tube 30 cm. long which is filled with garnets and bits of porcelain and cooled with ice. The gas is measured by the amount of water delivered by the syphon bottle which induces its flow. After passing 2 to 5 liters of gas the tube is washed out by drawing pure air through it and finally is washed into a beaker with

water to remove the SO_3. This is then determined gravimetrically by precipitation as $BaSO_4$.

In a modification of this method[103] the apparatus is similar but the absorption tube is washed out with water containing a known amount of 0.1 N iodine and the excess is titrated with 0.1 N sodium thiosulfate. A final titration is made with 0.1 N caustic soda, using methyl red as indicator, and the amount of SO_3 determined by difference.

The SO_3 content of the burner gas can also be found by Reich's method, in which the SO_2 content is determined by reaction with iodine and the total acid in an equal volume of gas by absorption in standard NaOH solution. The difference gives the percentage of SO_3.

The generally accepted place to sample the gases is in the main pipe between the cooler and the absorption apparatus.

Besides these chemical tests it is customary to record the temperature of the gases as they leave the combustion chamber and again after passing the cooler. Some form of recording pyrometer is desirable for the former work while an ordinary chemical thermometer is satisfactory for the latter.

Raw and Cooking Acid. The raw acid from the towers or tanks can be readily analyzed for its total, free, and combined SO_2 contents by several methods.

The total SO_2 is commonly determined by titration with iodine using starch as the indicator. A 1-cc. sample of the acid is pipetted into an Erlenmeyer flask containing about 100 cc. of water, a few drops of starch solution are added, and 0.1 N iodine is run in until the blue color appears. The total SO_2 in grams per 100 cc. (usually called per cent) is found by multiplying the number of cubic centimeters of iodine used by 0.3204.

The free SO_2 content of the acid is often determined by titrating a 1-cc. sample with 0.1 N caustic soda using phenolphthalein as the indicator. The free SO_2 in grams per 100 cc. is found by multiplying the number of cubic centimeters of alkali used by 0.3204.

The combined SO_2 is the difference between the total and free SO_2.

The analysis for total and free SO_2 just described is known as Winkler's method. When the two analyses are carried out on one sample, the method is known as that of Höhn.

For greater accuracy larger samples can be taken or a larger sample can be diluted in a volumetric flask and an aliquot portion taken. Sieber[93] has shown that the presence of CO_2 in the caustic soda solution may lead to errors of 5 per cent or more in the free SO_2, while Öman[73] found that CO_2 in the acid will also interfere with the titration when phenolphthalein is the indicator.

Another method of analysis, in which the presence of CO_2 does not interfere, is that of Sander, adapted by Miller and Swanson.[66]   A 2-cc. sample of the acid is first titrated with 0.125 N sodium hydroxide using methyl orange as indicator, an excess of a saturated solution of mercuric chloride is added, and the solution is again titrated with sodium hydroxide. The total SO_2 is equal to 0.4 times the second titration figure, while 0.2 of the difference between the two titrations gives the combined SO_2.

In the method devised by Palmrose[74] for mill control use, a 2-cc. sample of the acid is first titrated with 0.125 N potassium iodate to give the total SO_2, then with sodium hydroxide to give the free SO_2.

Jackson and Parsons[42] suggest sodium chlorite as the analytical reagent for determining the total SO_2, and in a method recently proposed by Kobe and Burke[54] it is determined by titration with calcium hypochlorite solution.

The cooking acid contains lignin derivatives from the .relief and is more difficult to analyze for its content of total, free, and combined SO_2 than the raw acid. Because of the presence of organic acids, titration with sodium hydroxide does not determine the free SO_2 accurately. Titration with iodine to determine the total SO_2, and the Sander method for the combined, or the Palmrose method with certain modifications for taking care of the reversible SO_2, serve satisfactorily for the analysis of cooking acids containing moderate amounts of lignin derivatives.

Sulfates in the liquor may be determined by placing 10 cc. in a covered beaker, adding an excess of strong hydrochloric acid, and boiling for some time until the odor of SO_2 is no longer noticeable. The sample is then diluted and the SO_3 determined gravimetrically as $BaSO_4$. Sieber,[94] who objects to this method as giving too high results because of oxidation of the SO_2 to SO_3, prefers to determine total sulfur by oxidizing with iodine or hydrogen peroxide and precipitating by $BaCl_2$, and from the SO_3 thus found deduct that corresponding to the SO_2 found by titrating with iodine. Oxidation can be eliminated also by displacing the air above the liquor with CO_2 before adding the hydrochloric acid and carrying out the boiling to remove the SO_2 in an atmosphere of CO_2 according to the method of Sherrard and Blanco.[90] Partansky and Benson,[75] however, consider the use of CO_2 an unnecessary refinement.

The bases in sulfite liquor are not often determined, but if values are needed the usual methods of analysis for calcium, magnesium, and sodium can be applied.[104,30]

Cooking and Waste Liquor. The analysis of the liquor during the progress of the cook is made difficult by the presence of organic acids and reducing sugars, by SO_2 combined with organic substances, and by the buffering action and color of the lignosulfonic acid. The common routine liquor tests are determinations of the total SO_2 by titration with iodine on either hot or cooled samples and observations of the color of the liquor. Color standards for comparison with liquor samples may be prepared by boiling coffee in water, cooling the solution, adding a little chloroform as a preservative, and diluting it until it matches the liquor from a cook which was known to be satisfactory. Color standards have also been made up from oil and iodine solutions. A recently developed instrument, the transometer, employing a photoelectric cell, is reported to be useful for measuring the color of liquor samples.

The Sander method has been reported by Miller and Swanson as satisfactory for determining the combined SO_2 up to the end of the cook, but the Palmrose method is not considered satisfactory for these liquors.   .

Mitscherlich's ammonia test has been used to indicate the lime present toward the end of the cook. In this test hot sulfite liquor is added to a graduated tube containing concentrated ammonia in the amount of 1/32 of the tube. When the calcium sulfite precipitate reaches 1/32 of the tube, or still better a constant amount, the cooking is considered to be finished.

In a control test recently described by Haider[35] the pulping is followed by measurement of the lignosulfonic acid content of the cooking liquor. This test is carried out by measuring the refractive index of the liquor sample with an immersion refractometer and determining the pulping degree from predetermined tables and curves relating refractive index and pulping degree to grams of calcium lignosulfonate per 100 cc. of liquor.

In some mills the end of the cook is ascertained from pulp samples blown periodically from the digester. These samples are then subjected to a rapid bleachability determination in order to measure the degree of .delignification or pulping. This procedure thus affords a more direct test than any test made on liquor samples. Its reliability depends largely upon obtaining a representative sample.

Sulfite waste liquor, because of its various uses as already outlined, is often subjected to more extensive analysis than the cooking acid or liquor. Partansky and Benson[75] have devised a system in which the following factors are determined: total solids; residue on ignition; calcium; sulfur as total sulfur, sulfates, free SO_2, loosely combined SO_2, and sulfone sulfur; organic matter; minor volatile constituents as

methanol, ethanol, and acetone; furfural; pentosans and pentoses; lignin; and sugars.

Life of Sulfite-Mill Equipment. The equipment used in making sulfite fiber is often subjected to even worse conditions than those in sulfate mills. The best opinions available from several sources have been combined in Table 38, which shows the probable life of each unit.

TABLE 38

Equipment	Probable Life	Cost of Annual Repairs
	Years	Per cent
Conveyor drive and structure..................	12–15	10
Conveyor chain...............................	6	20
Chippers......................................	12–15	15
Chip screens — shaker type...................	15	10
Digesters	At least 40	1
Digester linings..............................	7–10	3
Digester blow-off pipe (Extra heavy cast iron)....	7	2
Digester valves and fittings (acid-proof bronze)...	6	10
Blow pits (wood).............................	12	5
Gas relief pipe (extra heavy copper)............	6	8
Relief coolers................................	5	.
Sulfur burners...............................	20	4
Combustion chambers.........................	12	10
Combustion chamber linings...................	6	..
Cast-iron pipe between burner and cooler........	10	..
Gas coolers (burner gas).......................	15–20	5
Acid system (concrete towers).................	50	1
Acid system tower linings.....................	7–10	8
Acid-storage tanks (wood)....................	8–12	5–7
Acid-storage tanks (concrete, tile lined)..........	28	1
Acid pipe, lead...............................	6	8
Acid pumps..................................	3–10	20
Bronze reversing pumps for Jenssen towers.......	5	..
Strong acid pumps for same...............	2	..
Screens — centrifugal.........................	12	5
Screens — flat...............................	15	6
Stock pumps..............................	12	3
Stock pipe...................................	10	3
Bleach tanks, concrete........................	30	1
Agitators on bleach tanks.....................	12	5
Drainers — concrete..........................	50	1
Wet machines................................	10–12	5

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CHAPTER VII

GROUNDWOOD OR MECHANICAL PULP

H. J. ROWLEY

The preparation of groundwood pulp involves little of a chemical nature, yet its close relationship to the rest of the industry makes it desirable to include a short discussion of the general principles involved and the manufacturing methods and equipment employed. With increasing demands for high-quality pulps, more use is now being made of physicochemical and biochemical knowledge in this largest branch of the pulp-producing industry.

As early as 1844 Charles Fenerty of Halifax, Canada, had produced paper in small amount from pulp made by pressing wood against a revolving grindstone, but the demand for such pulps was very limited, and consequently development in mechanical means of securing them lagged. It was not until 1867 that the first sale was made of any considerable quantity of such pulp, manufactured in North America. This was produced by the Pagenstecher brothers and sold to the Smith Paper Company of Lee, Massachusetts. The pulp is said to have sold for eight cents a pounds and to have been made on two Voelter grinders secured from Germany.

Since then production has pyramided. In 1937 the world's production of all grades of pulp from wood was over 26,000,000 air-dry short tons, of which 10,413,000 tons were made by purely mechanical processes and known in the English-speaking world as groundwood or mechanical pulps. Of this production, 3,309,000 tons are attributed to Canada, 1,582,000 tons to the United States of America and 1,272,000 tons to Germany. Sweden, Finland, Norway, the Union of Soviet Socialist Republics, and Japan each contributed in the order noted amounts ranging from 750,000 to 400,000 tons. During the same year the world's paper mills produced nearly 9,000,000 tons of newsprint paper in which approximately 7,200,000 tons of these mechanical pulps were used, or 70 per cent of the total made. A variety of products as tissues, wall papers, cheap book and writing papers, rotogravure, wall and insulating boards, molded objects, and others consumed the remainder.

The present methods of manufacture are basically the same as in 1867, except for increased size and capacity of grinders. The rapid

223

improvement in pulp quality in the past two decades is due to refinements in stones and in means and methods of preparing the stone surface, to the contributions of many investigators on controllable operating variables, and to the increase of technically trained operating personnel. Today carefully produced mechanical pulp is a papermaking fiber, whereas at its inception, and for years following, the process yielded at best a flourlike material serving as a filler.

In recent years much effort has been directed toward securing mechanical pulps from wood by such means as chipping, shredding, or shaving the logs and subjecting the intermediate product so obtained, with or without the application of steam, to the action of refining engines. Although pulps suited to insulating or building board manufacture have been produced, no mechanical process yet has been evolved which can equal for paper furnish purposes the product of the grindstone, a unit which at one pass reduces logs to a defibered mass, at least 95 per cent of which is acceptable for news, tissue, and other paper demands.
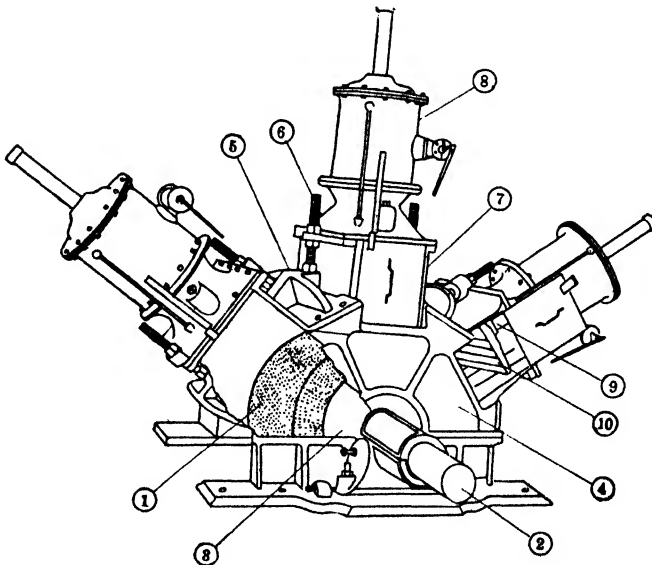
FIG. 31. THREE-POCKET GRINDER.

(1) Grindstone. (2) Shaft. (3) Steel flanges. (4) Casings or side frames.
(5) Bridge-trees. (6) Studs to support. (7) Pockets. (8) Hydraulic cylinders.
(9) Piston rods. (10) Pressure foot.

Grinders. In modern practice four types of grinders are in common use — the pocket grinder, the hydraulic magazine grinder, the con-

tinuous chain grinder, and the Great Northern and Kamyr types employing in varied combination the good features of the preceding three. In all, the pocket is built about the grinding stone, thereby confining the wood so that pressure, either hydraulically applied by means of pistons or mechanically through continuously moving chains equipped
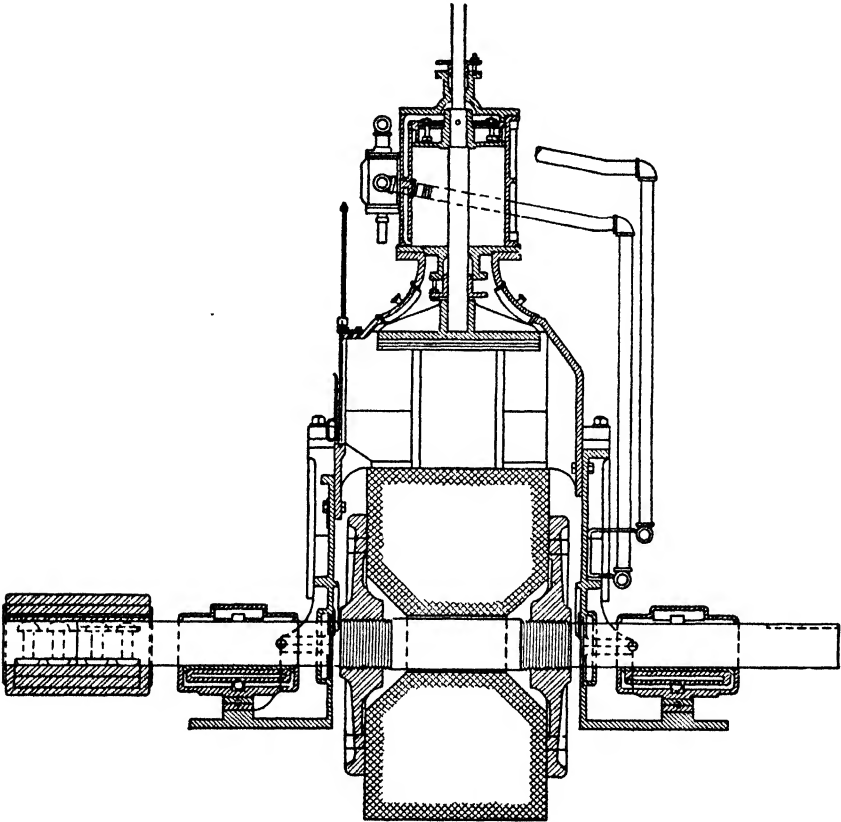
FIG. 32. THREE-POCKET GRINDER SECTIONAL ELEVATION.

with projecting dogs or edges, may press the wood against the grinding surface. Equally good pulps are made on all four classes by experienced operators.

With the three- or four-pocket grinder (Figs. 31 and 32), operation is intermittent and labor cost is relatively high owing to the method of charging the wood.

During the early years of this century the Voith Company experimented with grinders of a practically continuous type. Of these, the
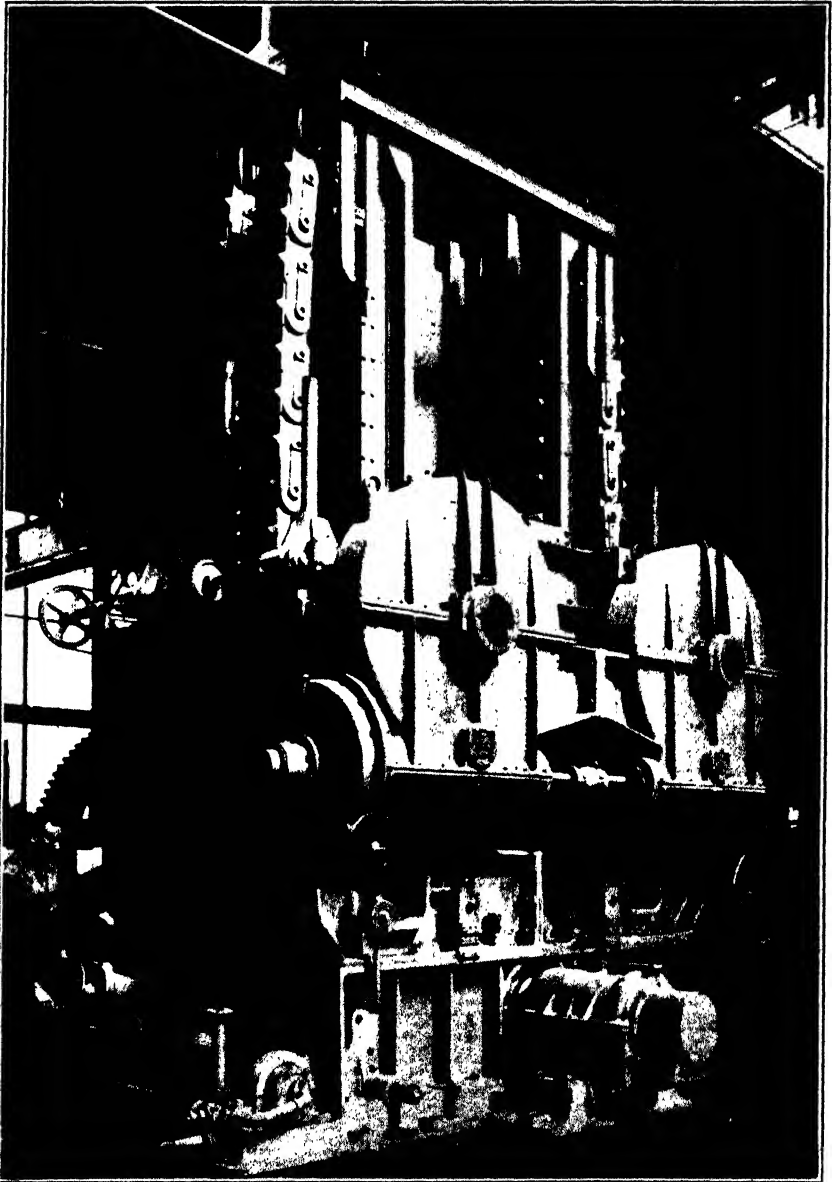
Courtesy of J. M. Voith Company.

FIG. 33.   CONTINUOUS-CHAIN SUPERGRINDER.

hydraulic magazine grinder proved successful and was first operated in 1910. These grinders, and also the continuous or chain type, are usually installed in pairs, the motor required to drive one pair usually ranging in size from 2400 to 4200 hp. To maintain as steady a load as possible on the motive power, the hydraulic pocket grinders are equipped with a timing device permitting only one pocket out of the four to fill at one time — an operation requiring less than 30 seconds — so that the load at no time falls below 75 per cent of maximum. This 25 per cent difference is even further reduced by other governing devices.

FIG. 34. CHARGING FLOOR. CONTINUOUS-CHAIN-GRINDER INSTALLATION. Finland.

More fully continuous operation with constant speed and load was attained by Voith in 1912 when the first continuous grinders went into operation. In these units (Fig. 33 and 34) the wood is placed in a central magazine over the stone and is fed downward by specially designed chains and dogs running in grooves down two sides of the magazine. The chains are electrically or hydraulically operated.

The hydraulic magazine grinder is shown in Fig. 35. It consists of a pair of high magazines located symmetrically about the vertical center line and has two hydraulic cylinders with wood pockets placed almost diametrically opposite each other. The stone sharpening

mechanism is hydraulically operated and placed in the space between the two magazines.

Hydraulic magazine and continuous-chain grinders are usually installed in two-story buildings of suitable height to accommodate the high magazine. All wood handling is done on the second floor and varies in method in different installations; the net result is a very neat
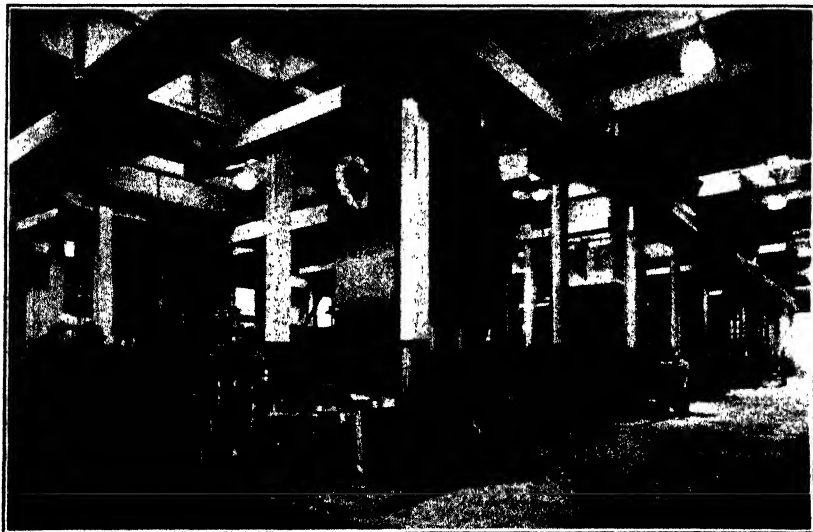
FIG. 35. OPERATING FLOOR. WATEROUS HYDRAULIC MAGAZINE GRINDER
INSTALLATION. Canada.

grinder room and a minimum of attendance. The obvious advantage of these units has led to a demand for a large grinder of less height, capable of being installed in existing one-story grinder rooms.

Efforts to enlarge upon the design of the older pocket grinder, even for 48-inch wood and 60-inch diameter stones, have been only partially successful. Such units still possess the inherent shortcoming of being hand fed and so requiring a large amount of labor per ton of product. This led to the designing of several types of low-head hydraulic grinders, so built as to be readily supplied by conveyors adjacent to low magazines or pocket openings. One of these, developed by the Great Northern Paper Company and hence known as the Great Northern grinder, is shown in Fig. 36. It has two pockets on opposite sides of the stone, each pocket being served by two pressure cylinders in parallel. The pockets, of sufficient width to take 48-inch wood, are open at the top. This grinder is similar in output and power requirements to the magazine and continuous types.

A second low-head type of grinder now in operation is the Swedish-designed Kamyr, continuous hydraulic unit. This has two twin cylinders on opposite sides of the stone. By means of a system of dogs, pressure is maintained on the wood while the pressure foot is retiring to receive another charge, thereby paralleling the chain grinder in continuity of operation.

Courtesy of Montague Machine Company

FIG. 36. GREAT NORTHERN GRINDER.

Very recently the Voith Company has installed in Germany, Finland, and France massive continuous units of the chain type, for wood of 1-meter length. These have given satisfactory operation, with daily productions of 50 to 55 tons. High peripheral speed of 4100 to 4700 feet per minute, large grinding area, and pressures of 40 to 50 per cent in excess of those usually employed account for the high output. One such unit is illustrated in Fig. 33. These new supergrinders are singly driven by motors of 2500 to 3000 hp.

Stones. Depending upon the grinder and the length of the wood used, stones vary from 54 inches in diameter and 27 inches face to the large stones of the new Voith grinders having a diameter of 71 inches and a face of 49 inches. The usual hydraulic magazine and continuous-chain types for 48-inch wood are equipped with stones from 62 to 67 inches in diameter and of 54-inch face.

Stones are of three main classes: (1) natural sandstones; (2) segmental artificial, with vitrified bond, as the Norton and Carborundum;

(3) monolithic artificial, with cold cast bond, as the Hercules, Ideal, and Sampo of German, Austrian, and Finnish manufacture, respectively.

As the size of grinding equipment has increased it has become more and more difficult to secure natural stones possessing freedom from flaws, and of the uniformity in grit and bond characteristics desired. With artificial stones, whether vitrified or cold cast with cements, any predetermined grit range is possible, bond or matrix characteristics may be controllably modified within a reasonable range, and uniformity throughout the stone is assured.

It is fairly well established that, when proper selection is made of either artificial type, the pulp produced is comparable in quality to that secured from natural stones, and the stone cost per ton of pulp made during the life of the stone favors the artificial type. In America when artificial stones are chosen the segmental vitrified variety is preferred; in Europe, the monolithic cold cast type.

Stones of the vitrified type are made of segments assembled about a solid, well-reinforced concrete core, the joints between segments being filled with one of the newer plastic bodies or with white metal of suitable composition. Stones are available with a variety of grits or cutting particle sizes, and with different hardness or toughness in the binding medium. In the Norton stone the grit particles are of silicon carbide (Chrystolon); while those of the Carborundum Company are of aluminum oxide (Alundum).

In the classification of naturally occuring stones such terms as hard, soft, coarse, medium, or fine are generally employed, but sometimes these terms are not correctly or aptly applied by those making judgment. The so-called fine stones, for example, contain considerable proportions of coarse material and may seem fine because of the density of their structure, whereas another stone of similar grit analysis might be visually classed as coarse because of a more open texture.

A hard, natural stone may really be thought of as one in which the bond is so tough and resistant that it retains the grit or cutting particles so tenaciously that the stone does not quickly wear away even under severe grinding action. A stone from which these particles are easily broken away is called soft. Considered from another angle a dense stone in which the spaces between the grit are thoroughly filled with finer particles and bond will act as if it were " harder " than a more open one, even though the actual measured degree of hardness is the same. Such a stone will also hold its burr impression for a longer time in operation than one less dense.

To determine satisfactorily the degree of fineness or coarseness of natural stone a screen analysis should be made on a carefully chosen sample. Two generally accepted methods of preparing the sample are employed, both of which unavoidably break some of the grit particles. One is to heat the sample, of about 100 grams, to a red heat in a muffle and then quench it quickly in cold water. This breaks down the bond and permits the stone to be crumbled easily and the individual grits separated. The second method is to break down the unheated sample very carefully with mortar and pestle. Simons and Bornstein,[4] using the second method to prepare the sample and classifying various natural stones from Ohio, West Virginia, Canada, and England, show the screen analyses in Table 39.

TABLE 39

Type of Stone*	Percentage Retained						
	Size of Screen — Meshes per Linear Inch						
	20	28	35	48	65	100	Pass
Fine.....................	0	2	30	30	16	10	12
Medium fine.............	7	12	35	19	10	7	10
Medium coarse...........	26	12	24	19	8	5	7
Coarse..................	45	10	20	10	5	5	5

Stone Surface. The condition of the stone surface depends on several factors, among them being the size and sharpness of the individual grits, the ease with which the binding material wears away, and the manner of dressing the stone. This last is the most important single operation in the production of groundwood, and the quality of the pulp produced depends on the judgment of the burr man or jigger man who is responsible for this work. Dressing, or burring, is performed by working across the face of the stone small, hard, steel rolls, or burrs, of various designs which roughen the surface and leave on it a definite pattern, varying with the burr employed. Much attention has been given to the design of these burrs, which are in reality rotary cold chisels, and appreciable improvement in their performance has resulted. It can be generally stated, however, that, if the surface is brought to the same condition of sharpness of grit, practically the same quality of pulp can be obtained under like conditions of pressure, speed, and temperature, regardless of whether the design of the markings is straight cut, spiral, or diamond. This possibility depends very largely on the ability of the operator in charge of burring to assess correctly the characteristics of the stone and to apply the type and depth of

dressing necessary to secure the desired pulp quality with the conditions of stone speed, pressure, pit consistency, and temperature employed. The question of surface dressing of the stone is today's most important groundwood problem, as it is on the stone-wood interface that the pulp is truly made.   Much study is now being devoted, especially in Canada, to methods for obtaining with more certainty surfaces better adapted to the production of more uniformly long groundwood fiber, containing less wood flour than that now made.

Grinder Output.   Production per grinder varies from 6 to 12 tons per day with the usual pocket grinders to 20 or 25 tons with the larger magazine units in common use.   The new European supergrinders, as already noted, produce 50 to 55 tons.   This variance in daily output is due to the length of log ground; to the pocket area or stone grinding surface exposed continually to the wood; to the pressure applied to the wood; to the coarseness or fineness of the stone surface; to the peripheral speed of the grinding stone; and to the density of the wood employed.

Pulp Flow.   The pulp coming away from the stones collects in pits under the grinders and from there flows to coarse or bull screens, with $\frac{1}{4}$- to $\frac{3}{4}$-inch perforations, which remove slabs, knots, and large splinters. For satisfactory operation of these screens the stock should be diluted to at most 1 per cent dry matter.   The stock passing the coarse screens goes next to screens of the centrifugal type or in rare cases of the flat diaphragm type.   Depending upon the screen employed, or the pulp quality and capacity desired, the stock is diluted with white or back water to 0.6 to 0.25 per cent dry.   It is desirable that the diluted stock be passed through a riffler or over a sand settler before going to the screens as much wear on the latter is thus avoided.   The screened stock is then thickened to the desired consistency, usually about 3 to 4 per cent, by means of " deckers " or filters and routed through storage tanks directly to the proportioning system of the paper machine, or immediately after screening to wet machines to be converted into lapped pulp.

The consistency of the stock at various points demands careful attention and control, as on this control, or " stock running " as it is termed, depend in large measure the quality of the pulps secured and the quantity of screenings rejected.   After the grinder, water is the conveying medium for the pulp during its various stages of screening. This must be removed ultimately, so it is advantageous to operate at as high consistencies as possible.   Screens such as those equipped with pulsators, which operate at ranges between 0.6 and 0.7 per cent dry matter, require subsequent dewatering equipment of half the capacity needed by those which operate at consistencies of about 0.3 to 0.35

per cent. Cleanliness and other quality factors, however, must be taken into consideration and a proper balance maintained between economy and quality in making choice in such questions. Consistency at various points in an average groundwood mill is given by Brawn[1] as in Table 40.

TABLE 40

Location	Consistency, Per Cent Bone-Dry Basis	Pounds of Water per Pound of Stock
Wood to grinders.....................	60	0.67
Stock from grinders..................	5.5	17.2
Stock to bull screens.................	0.75	132.0
Stock to centrifugal screens...........	0.38	262.0
Accepted stock from screens...........	0.30	332.0
Stock to deckers and wet machines......	0.30	332.0
From deckers to paper mill or storage tank...............................	4.00	24.0
Stock from wet machines, in lap form....	32.00	2.1
Rejections from centrifugal screens......	1.00	99.0
Rejections to tailings screens...........	0.40	249.0
Accepted stock from tailings screens.....	0.10	999.0
Rejected stock from tailings screens.....	0.80	124.0
White water from deckers and wet machines...........................	0.04	2499.0

Power Requirements. In mills where electric energy is purchased, the cost of power per ton of pulp made is an important item in total cost — probably second only to that of the wood employed. The striking feature of mechanical pulping is that such a high proportion of the energy consumed appears in the system as sensible heat. Campbell[3] states that at least 99.9 per cent of the input energy can be so accounted for. It may be that some of this heat plays a useful role by softening the fibers just prior to their removal and thus aids in their separation. On the other hand, by rendering the wood more plastic, the energy consumed in removing fibers may be actually increased.

In America, in the production of groundwood pulp of newsprint grade, from 60 to 70 hp. days per ton are consumed by the grinder, whereas for a similar grade in north Europe, because of higher grinding pressures and other contributory factors, 50 hp. or lower is used. For coarser pulps than those accepted for newsprint, as for wall board, less power is consumed, whereas for finer grades as for tissues and rotogravure as much as 75 or 80 hp. days per ton may be required.

The power per ton of pulp varies inversely with the sharpness of the stone, while production varies directly with sharpness. Immediately

after a stone is sharpened, therefore, the rate of production is high, and the power consumed low, but as the stone becomes dull the production decreases and the power consumed increases. A freshly sharpened surface, and in particular one on which the burr has been deeply pressed, produces pulp of low strength, high freeness, and high screenings loss, while pulp of higher strength properties, lower freeness, and lower tailings is produced by a less sharp stone, but at a greater application of power per ton of pulp made.

Pit Temperature and Consistency. The effect of the temperature and consistency under the grinder at which mechanical pulp is produced was for some years a controversial point between European and American manufacturers. The general American practice is to operate at high temperatures, up to 190° F., and at consistencies ranging from 4 to 8 per cent. It has been claimed that fibers so produced are longer, stronger, and work " freer " on the paper machine. In the past, European mills worked at much lower temperatures, the claim being that cold-ground pulp is finer and freer from shives, and gives a better closed sheet of greater opacity than does hot-ground pulp. Today, however, European mills producing groundwood for news machines, at least those operating at speeds of 1100 to 1400 feet per minute, have approached more nearly the higher temperatures, and values of 150 to 155° F. are now not uncommon. Their pit consistencies still remain low, ranging from 1 to 1½ per cent leaving the grinders.

TABLE 41

PULP TEST DATA

Character	Pulp		
	1	2	3
Freeness — Canadian standard.........	82	80	80
Drainage time, seconds...............	11	13	12
Burst factor........................	16.8	16.2	17.1
Tear...............................	0.74	0.78	0.73
Breaking length, meters..............	2740	2800	2810
Bulk...............................	2.15	2.22	2.25
Oil penetration, seconds.............	211	218	218
Water absorption, per cent...........	116	115	131
Porosity, seconds...................	24	21	24

Recent comparisons of Canadian and north Europe pulps of news grade show little of the earlier fineness, strength, or freeness differences. Table 41 compares a north Europe pulp — No. 1 — with two from different Canadian mills. All were made in 1938. No. 2 is largely

balsam, while the others are from spruce. All were screened and thickened in the mills of origin and sampled at the point of admission to the paper machine system.

Further comparisons, in a second laboratory on different pulps, and employing somewhat different methods of testing, gave results of which the data in Table 42 are typical.

TABLE 42

PULP TEST DATA

	Pulp				
	1	2	3	4	5
Freeness, Canadian standard..........	87	81	94	116	105
Burst factor........................	12.7	10.9	11.8	11.1	11.9
Tear..............................	0.42	0.40	0.41	0.42	0.39
Bulk..............................	2.84	2.54	2.87	2.65	2.74
Classification					
Retained 28 mesh..................	8.9	7.3	13.4	9.2	10.8
" 48 "	16.2	15.5	15.9	17.7	18.5
" 100 "	23.1	22.5	22.0	23.2	21.3
" 200 "	9.1	9.9	8.1	10.4	9.8
Pass 200 "	42.7	44.8	40.6	39.5	39.6

Pulps 1 and 3 are Canadian and the others European. Numbers 1 and 2 were screened and thickened in the mills of origin; Nos. 3, 4, and 5 were grinder pit pulps, screened on a single plate, laboratory flat screen before making all the tests except that on the Johnston classifier. The classification of these three unscreened pulps enables a comparison to be made with the screened samples. Pulps 1 and 3 were composite samples from 20 hydraulic magazine grinders (Waterous), 10 of which were equipped with Norton artificial stones and 10 with natural sandstones. Pulps 2, 4, and 5 were made on continuous-chain grinders using Sampo stones; No. 5 was made on one of the new Voith supergrinders at a rate of 50 short tons per 24 hours.

Woods Suitable for Groundwood. Almost any kind of wood can be made into groundwood pulp, and the resulting fiber will possess properties depending on the characteristics of the wood from which it comes and on the care and intelligence employed in its making. Spruce and balsam fir have been most frequently used and are still considered best for the production of the highest grades of mechanical pulps. As with all woods they give most satisfactory pulps when green or thoroughly wet.

Jack pine, hemlock, white pine, southern pines, gumwoods, eucalyptus, birch, and poplar are being used today, each species in large

measure satisfying certain quality and use demands. Formerly one grade of groundwood met nearly all requirements, but today each product demands its own quality of pulp, and that which is satisfactory for one may be entirely unsuited for another.

Pretreatment of Logs.   The changes induced by boiling or steaming the wood before grinding very profoundly influence the pulp obtained. Its color is generally darker than that from unsteamed wood, and the fibers are much longer, better separated, and stronger. The changes in the pulp are practically identical, provided the cooking time and temperature are the same, whether the logs are steamed, or boiled while immersed in water. Steaming has the advantage over boiling in that less heat is necessary and the condensed liquors are drawn off in concentrated form, which is a benefit if recovery of by-products is attempted. As soon as steaming starts, the formation of acid commences and increases up to the end of the treatment. Both acetic and formic acids are produced, in the ratio of 6 acetic to 1 formic, necessitating, if color is important, the employment of retort linings resistant to those acids at the concentrations encountered.

Temperature and the duration of treatment are important factors to control, because of their influence on the color, strength, and yield of pulp. Increasing both time and temperature increases the strength of the pulp but makes it darker in color, while the ultimate yield is decreased because of the increased rate of hydrolysis of wood substance at elevated temperatures and the greater solvent action of the water.

Boiling for 3 hours at 115° C. even with superimposed pressures of 50 pounds per square inch, as secured by pumps, causes but little change in yield, color, or grinding power requirements. An increase in either time or temperature appreciably beyond these values induces degradation in both yield and color. Trouble from " pitch " is relieved appreciably by pretreatment, the easement being most soundly attributed to the loss of volatile substances, as turpentine and related bodies, which if present and in contact with the wood resins cause them to remain tacky in the pulp.

A study of the grinding of steamed or boiled wood has brought out a number of interesting facts. The power required per ton of pulp increases with the intensity of pretreatment and may reach a value at least 25 per cent in excess of that required for similar untreated wood. This is not because the softened wood is harder to grind, but rather paradoxically because it is easier to pull apart in fuller length the fibers whose ligneous bonds to neighboring fibers have been greatly weakened by the treatment. Under normal grinding conditions a much too coarse and free pulp is secured. To keep the pulp within the free-

ness bounds set by the paper machine requires a comparatively smooth stone, low pressure, or both, with the resultant high power consumptions per ton of pulp connected with such conditions of grinding. Spruce logs 2 feet long and averaging 6 inches in diameter, when boiled for 3 hours at 125° C. and ground under *ordinary* conditions of pressure and stone surface for untreated wood, will readily produce pulp of over 300 freeness, Canadian standard. This is at least 150 points too high for even a one stock news furnish, unless refining in an efficient unit is resorted to.

Although over a period of years a large tonnage of newsprint has been made from steamed or boiled wood with little or no sulfite pulp, the plan has not been adopted in large-scale operation, largely because of the high capital cost involved in installing the new equipment necessary in existing mills and because of other expenses attending such a process change. An appreciable tonnage of thoroughly steamed and highly colored brown pulp, however, is made and converted to a variety of other products, as box boards, and bogus kraft for wrappers and covers.

Tests of papers made from steamed and unsteamed woods show that the steamed pulps give a higher percentage of stretch than the unsteamed, even though the unsteamed are mixed with 20 per cent of sulfite fiber. Like chemical pulps, steamed groundwood is considerably influenced by beating, variations in which cause marked variations in the strength of the paper. Paper produced from steamed or boiled groundwoods, particularly from the hardwoods, shows the characteristic water-resistant qualities and hardness of hard-sized papers.

Quality Control. With any method of grinding close control is essential if a uniform product is to be made. Two instruments for this purpose stand out because of their utility and simplicity — the blue glass and the freeness tester.

The blue glass is of single diamond thickness, 8 to 12 inches square, set in a wooden frame about 1 inch high. On the glass is placed a suspension of the fiber to be examined, at about 0.1 per cent consistency. From the visual impression secured an experienced operator — but only an experienced one — can very closely evaluate the properties of the pulp examined. In most mills the blue glass is in continual use.

The freeness tester has been described many times. Its operation is simple, but for accurate work great care is necessary in determining the consistency and temperature of the pulp suspension used. Instruments in general use for determining freeness include the Canadian standard, the Green, the various Williams units, and the Schopper

Riegler. For the Canadian tester a consistency of 0.3 per cent and a temperature of 20° C. are recommended. Correction curves to care for determined deviations from these values in practice must be resorted to for accurate evaluations of freeness. For process control, freeness tests are made half hourly or hourly on stocks secured from some one control location in the system, as after the coarse screens or after the fine screens.

Since the introduction of the British sheet-forming machine this has had a limited use in determining the drainage time and drainage factor of groundwood pulps, according to the method recommended by Campbell.[2]

Other methods having a limited acceptance for occasional or research use include the sedimentation tester, the various instruments for projecting fiber outlines on screens, either stationary or in motion, and various screen classifying instruments. None of these has met the general acceptance of operators as a control means as have the blue glass and the freeness machine.

Slime and Decay. Decay of moist groundwood while in storage in lapped form has long been a problem of importance. Similarly the formation of slime growths in the groundwood system itself has been the cause of much study and the source of great inconvenience and loss. These have often been regarded as happenings surrounded with a great degree of mystery, but they are definitely natural phenomena and to be expected under the conditions that have existed and still exist in mills. Many who would expect other materials of vegetable origin to decay rapidly under similar circumstances of time, moisture, and temperature are often perplexed that suspensions of lignocellulose and dilute solutions of wood sugars should admirably suit the diet requirements of a multitude of air-, water-, or wood-borne bacteria and algae.

Poisons have been and still are employed with increasing success, as better understanding and identification of the injurious organisms are secured, and as chemicals of greater or more selective toxicity are introduced. No poison, however, will take the place of scrupulous cleanliness, particularly in those places not exposed to continual inspection.

In grinding at high temperatures, although the time of exposure is not long, a high degree of sterilization is effected, and many organisms perish. Spores, however, may survive and assert themselves as mature organisms later in the system. The water employed, unless naturally sterile or possessing a residual of chlorine at least 15 minutes after dosage, may contribute many destructive bacteria or algae, varying in number and identity with the season or locality. Sterile water secured by known methods is the solution of this source of contamination.

It is difficult to cope thoroughly with air-borne infection, owing to the distance from their source that the organisms may be transported. An efficient and determined effort to prevent accumulations of decaying pulp matter in and around the premises is a definitely constructive step in the prevention of air-borne contamination.

In mills having internal slime difficulties relief has occasionally been secured by the use of chloramine either in the white water systems or in the treatment of raw water. The action is similar to that of elementary chlorine except that the effect of the chloramine is prolonged because of the slow release of the chlorine from combination. The efficiency of chloramine or of chlorine itself in the sterilization of groundwood or groundwood white water is problematical when one considers the rapidity with which chlorine combines with lignin and recognizes that this makes up 28 to 30 per cent of the solids present.

Various ions, as copper, zinc, mercury, silver, the arsenate and tungstate ions, and others, are definitely toxic to many of the slime-forming substances. Copper and zinc in the form of the sulfate and chloride, respectively, when used in white water dosage at a rate of $\frac{1}{4}$ pound per day per ton of pulp, have been found highly effective as a means of control in several large mills. Alternation in use of these two chemicals every two or three weeks has been found more satisfactory than the continual use of either.

Quite lately successful use has been made in wood preservation of chlorine-phenol and organic mercury derivatives, but no extended use of these is known in the groundwood decay problem. Yet it is believed that their use would be beneficial if the cost and their return in effectiveness should be found comparable.

Much of the difficulty experienced with slime, and general impairment in color, is traceable to poor or haphazard design in chests, launders, agitators, etc., permitting localized sluggishness and lodgment of fiber, and to the use of iron in pipes, pumps, and general equipment coming continually into contact with the stock. Cast iron and mild steel though satisfactory in initial cost and having advantageous mechanical properties are definitely inferior to copper and the newer ferrous and non-ferrous alloys for continued exposure to groundwood. These alloys are now available, and they dependably resist general corrosion and that irregularity in wear, or pitting, so characteristic of the more common iron and steel.

With care and foresight in initial design and choice of equipment or in subsequent alterations, it should be possible to approach more closely than at present those conditions of agitation and flow which will insure continuity of suspension and movement of stock in all parts of the

slush system. In this connection, it can be taken as axiomatic that the fiber which goes directly from the grinder to the machine does not contribute to internal slime conditions.

Apart from supplying pitted surfaces for lodgment of material which ultimately decays and breaks away, iron is also a cause of impairment in pulp color. The ligneous material of which groundwood is so largely composed is related in structure or chemical behavior to the tannins which, in combination with iron, give highly colored, dark bodies. These forming throughout the pulp mass tend to lower its color.

To some extent in this country, but more particularly in Europe, copper is replacing all iron piping, launder linings, and other surfaces exposed to pulp and white water, with gratifying results in slime abatement and color improvement. As already noted, alloys now available are and may be similarly employed.

Bleaching. Chemicals employed in brightening the color of groundwoods are reducing agents and change the colored bodies in the fibers to less highly colored ones. The brightening so secured is not permanent, and reversal occurs in a matter of months under normal atmospheric conditions. Sunlight causes rapid recurrence of the former shade.

In the production of bleached groundwood on the wet machine dilute solutions of calcium or sodium bisulfite are sprayed, dripped, or applied, by means of a wick fed from a trough extending across the machine, to the pulp web as led to the roll. The pulp so impregnated is cut and folded into laps in the customary manner. After a week or ten days' storage maximum brightness is attained at ordinary room temperature.

Sulfur dioxide, either dissolved in water or in the form of the raw acid employed in sulfite pulp manufacture, reacts readily with pulp in slush form, and increasingly so as temperature is raised. At a temperature of 180° F., as in the grinder pit, the brightening effect is almost instantaneous when addition is made at the rate of 20 pounds SO_2 per ton of pulp. Experience with this method, however, has proved unsatisfactory, as the bleaching effect is fugitive and disappears in a few minutes in the ordinary groundwood stock system.

Zinc hydrosulfite has been found an efficient bleaching agent when employed in quantities ranging from 10 to 20 pounds per ton of pulp treated. The end products of the reduction have been found very destructive to bronze equipment — screens, Fourdrinier wires, etc. — and where it is continually employed, the introduction of special corrosion-resistant washing filters has been found necessary. With this additional washing step zinc hydrosulfite is successfully used in

the bleaching of highly colored hemlock groundwood pulp for news manufacture.

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MISCELLANEOUS PULPING AND PULP-TREATING PROCESSES

E. Sutermeister

Although the great bulk of paper-making fibers is produced by the sulfite, sulfate, soda, and groundwood processes, a smaller amount is made by newer processes which are worthy of consideration. Some of these are merely modifications of older methods, while some are quite different in character. It is difficult to obtain much information regarding these processes, but it is believed that what follows is fairly descriptive of the most important which have been used or proposed. Many others are either such slight modifications of existing processes or so obviously the dreams of " kitchen inventors " that they need not be mentioned here.

Purified Fiber. This type of fiber, which was called alpha-fiber or alpha-cellulose when first sold in this country, is prepared from ordinary grades of sulfite or sulfate pulps by treatments which remove or reduce the ash constituents, resins, lignins, and the hemicelluloses, including polymerized carbohydrates, mannan, levulan, and pentosans. According to Jayme,[30] the ash substances may be greatly reduced by the methods employed in base exchange, while resins may be emulsified or dissolved with caustic soda and surface-active agents and then removed by washing. Lignin is fairly well taken care of by the usual bleaching operations, especially in multistage bleaching. Removal of the hemicelluloses is the step which causes the greatest change in the product, and very little can be found about this in the literature, except in patent specifications, and these are so voluminous and confusing that it is almost hopeless to obtain a clearly defined picture of the situation. A review of the more important patents up to 1928 is given by Rossman,[42] and reference is made to many of the more recent ones by Jayme.[80]

From the paper-making standpoint purified fiber is a bleached fiber of exceptional whiteness and high alpha-cellulose content. There is no fixed percentage of alpha-cellulose which will permit a product to qualify as a purified fiber, but anything above 93 per cent usually shows the paper-making qualities which are generally associated with this

product. The ordinary bleached sulfites usually contain 85.5 to 87.7 per cent of alpha-cellulose. In paper making, purified fibers impart softness characteristics closely approaching those of rag fiber, tearing qualities similar to those of kraft, as well as high bulk and good opacity and formation. These properties are modified by the cooking treatment given before the purification and by the kind of wood used. High alpha pulps from deciduous woods cannot be expected to have the strength of those from softwoods, but they are much softer and whiter than soda pulps.

According to Richter,[39] alpha-fiber owes its softness to the removal of pentosan groups and the elimination of hydrocellulose, which is unavoidably present when wood is cooked in an acid liquor. It resists hydration and does not make hard paper, even when beaten for a long time; it is therefore not good for such products as glassine, but is excellent where high opacity is desired and for waterleaf papers to be used in parchmentizing, vulcanizing, and laminating with resins. According to present accelerated aging tests the purified pulps appear to have the permanence of rag fibers. For most papers Jayme[30] recommends a relatively slight purification; for tough and very strong products a half-bleached kraft with an alpha-cellulose content of 93 per cent; while as rag substitutes products with a higher alpha-cellulose content are more satisfactory. In general these purified fibers find a greater use for dissolving purposes than in paper making.

The earliest methods of making alpha-fiber involved the use of lime. In a study of such a process Genberg[26] found that more than 5–10 per cent of CaO was unnecessary. When the pulp density was 4.5 per cent and the temperature 100–140° C., over 70 per cent of the total increase in alpha-cellulose content took place in the first 4 hours. The most important factor was the initial alpha-cellulose content; this should be as high as possible before starting the treatment with lime. Multiple treatments with lime have no effect on the alpha-cellulose content but increase the loss in weight. Almost the same alpha-cellulose content is given with 10 per cent of CaO or 5 per cent of NaOH, but the former gives a lower copper number and a greater loss in weight. Magnesia lime is no better than high-calcium lime.

According to Jayme,[30] modern refining processes may be divided into hot and cold groups, depending on the prevailing temperature during the treatment, and these may be subdivided into other combinations, as " hot-cold," " cold-hot," " alkaline-acid," and " acid-alkaline."

For the hot refining process, as applied preferably to partly bleached pulp, the highest practical limit for caustic soda is about 10 per cent

on the weight of the fiber, or its equivalent in other alkali. This would correspond to a concentration of about 0.5 to 1.0 per cent with stock consistencies of 5 to 10 per cent. Richter[40] states that to obtain an alpha-cellulose content of 94 per cent the treatment may be made within the following limits: pulp consistencies 9–12 per cent; caustic soda 5–8 per cent on the fiber weight; time of treatment 3 to 8 hours; and temperatures of 82° to 100° C. To produce a pulp similar to cotton, with an alpha content of 96 to 99 per cent, more severe conditions are necessary, and heating with alkali for 1 to 3 hours at 1 to 2 atmospheres pressure may be resorted to. Ross and Mitchell[41] found that when heating sulfite pulp in a digester for 3 hours the concentration of caustic soda over a range of 1 to 7 per cent had little effect at temperatures below 160° on the amount of material dissolved or on the alpha-cellulose content of the pulp produced. At higher temperatures the effect of concentration was much more marked, and for every temperature there was an optimum concentration of alkali which produced a maximum of bulking properties in the fiber.

After the treatment, enough alkali should be present to keep the fiber alkaline during washing, for which hot water is preferred to cold, as it gives a brighter product and a somewhat higher alpha content. The maximum alpha content by hot refining seems to be about 96 per cent. If the alpha content is raised from 87 to 96 per cent the theoretical yield is about 90 per cent, but actual yields are only 70 to 75 per cent. The final bleaching of the fiber should be under strongly alkaline conditions in order to prevent injury.

The cold refining process is preferably applied to bleached pulps and is carried out with caustic soda at high concentration, which, however, may be decreased as the temperature of treatment is lowered. Thus a 12 per cent solution is recommended at 20° C., while one of 8–9 per cent will do the work at 0° C. or one of 6–8 per cent at −10° C. The cold process is the only one which will give an alpha-cellulose content of 96.5 per cent or higher. It is best applied in conjunction with one of the alkaline pulping processes, since its successful operation demands efficient recovery of alkali. This is not true of the hot process, where no attempt at alkali recovery is made. Satisfactory conditions for the cold recovery process are: pulp consistency 5–10 per cent; caustic soda 72–228 per cent on the fiber weight, at concentrations of 8 to 14 per cent; time of treatment 1–2 hours; and temperature 0–20° C. Yields of about 85 per cent will be obtained.

The product is in the mercerized condition, but this can be avoided by carrying the process out in stages and operating the final one at such a temperature that mercerization does not occur. Cold refining

may be carried out in the presence of an oxidizing agent, with the production of so-called non-aging pulps, which can be made into viscose without going through the aging process. These should be of importance in both viscose and lacquer work. If higher temperatures (up to 60° C.) are used with this oxidizing mercerization the final bleaching is unnecessary and the pulp is very white.

A careful study of many of the factors influencing the refining process has been made by Rys and Bonisch.[45] They also divide the methods into hot and cold processes and in the former find that higher temperature, stronger liquor, and longer reaction time give higher alpha content, with the highest limit at about 96.5 per cent. A low alpha in the original pulp leads to low alpha in the refined product, and as a certain fiber stability is necessary for hot refining a partly bleached fiber is better than a fully bleached one. When extracting with caustic soda at 110° C. for 90 minutes a concentration of 1 per cent need not be exceeded.

The most startling statement in their paper is that the alpha-cellulose content gives no generally valid conclusions as to the actual purity of the fiber or its refining degree, in spite of which the authors draw conclusions from changes in the alpha-cellulose content of less than 1 per cent.

Chlorination Processes. The use of chlorine for bleaching was known at an early date, but it is not always clear whether elemental chlorine or hypochlorite was used. It appears that chlorine water, followed by an alkaline treatment, was used for bleaching by Berthollet as early as 1787, and it is stated by a writer in *Annales de l'industrie*, 1830, p. 503, that the method for preparing straw and esparto pulps with chlorine was first applied on a commercial scale in Russia. Cross and Bevan used it in their method for the quantitative determination of cellulose, and more recently two adaptations of the process have been worked out on a commercial scale. These started at about the same time, and both included the following four operations:

1. An alkaline pretreatment, or digestion of the raw material.
2. Chlorination of the predigested material.
3. An alkaline wash to dissolve the chlorinated products.
4. A final bleach with hypochlorite.

The deVains process used chlorine water for the chlorination step, while the Pomilio (or Cataldi) process employed gaseous chlorine. Both started as batch processes for the treatment of straws and grasses, but the deVains process proved unsuccessful, while the Pomilio process has developed into a satisfactory continuous method.

According to Clerc,[17] the deVains process required 10 to 12 hours for a complete cycle — charging, heating, cooking, relief, waste-heat recovery, two washings in the digester, and dumping. The digesting liquor contained 8 to 9 per cent of caustic soda on the weight of the straw at a strength of 12 to 14 grams per liter. The chlorination was carried out continuously in a gas-tight system into which the predigested pulp and chlorine water were pumped at a consistency of 5 to 7 per cent. The chlorine was nearly used up when the stock was discharged.

In 1922 six plants to use this process on straw, esparto, and bamboo were said to be under construction, but later information is that all were abandoned or changed to other processes. The Pomilio process, on the other hand, was said in the early part of 1938 to be established in three plants producing about 100 tons of pulp per day, and enlargements of these plants and the completion of four others which were under construction were expected to bring the daily production up to 266 tons.

The Pomilio process uses as raw materials salt, energy, and the fibrous raw stock. There is no prolonged pressure cooking and no alkali recovery, and the total energy required per ton of bleached pulp is usually less than that for a ton of groundwood. The process is flexible; the soda and chlorine used may be in the proportions produced by the electrolysis of salt, or one may be increased at the expense of the other to permit the sale of part of the more valuable product. The process is applicable to a wide range of fibrous raw materials from grasses to woods, and it yields products varying from semi-chemical pulps of the kraft type, through unbleached and easy-bleaching pulps to those sufficiently pure for dissolving purposes. Semi-chemical pulps may sometimes be made so cheaply as to compete with groundwood.

The alkaline digestion stage is much more important than the name of the process implies, and it would be better to call it the " soda-chlorine " process. The digestion is conducted by boiling with dilute caustic soda solutions at atmospheric pressure, or if the material is highly lignified, like wood, a digestion under pressure is desirable. For straws and grasses the caustic soda solution may range from 5 to 30 grams per liter, the ratio of solid to liquid from 1 : 3 to 1 : 6, and the time of digestion from 1 to 2 hours.

In the second stage the stock is treated with chlorine gas in the cold for a sufficient time to chlorinate the organic impurities, especially lignin. The chlorine may act by addition, substitution, or oxidation, or the three are more likely to take place simultaneously. More than half of the chlorine used may form HCl, so that the chlorination is under acid conditions. The addition reaction is most desired; substi-

tution entails a large chlorine consumption, while oxidation may injure the fiber. The ratio between addition and substitution chlorine depends on the nature of the raw materials and their non-cellulose constituents, while the amount of oxidation depends also on the operating conditions. Chlorination is rapid, and oxidation is not to be feared until practically all the lignin is chlorinated. Since danger of oxidation is greatest at about neutrality, acid formation is distinctly beneficial.

As soon as chlorination is finished the stock is given a wash with water to cool the mass and remove acid, and this treatment is followed by an alkaline wash to remove the chlorides which are insoluble in water. These include the larger part of the chlorinated compounds, the most important of which are the lignin chlorides with two to four chlorine atoms in their molecules. This alkaline wash gives an easy-bleaching pulp of high purity, even purer than the bleached pulp because of the presence of ash and oxycellulose in the latter.

The final step in the process is a light bleach, usually from 1 to 3 per cent of active chlorine being sufficient.

The present continuous process, which utilizes towers for both digestion and chlorination, is shown diagrammatically in Fig. 37. The tower for the alkaline digestion is of sheet iron, and that for chlorination is of tile-lined concrete. The material is fed in at the top, and when part way down it comes in contact with steam in the digestion tower, or chlorine gas in the other. The rate of flow of stock is regulated by " extractors " at the base of the towers; their duty is more that of determining the speed at which the stock falls than its actual removal from the towers. The towers are high enough so that the weight of material contained will crush the bottom layers over the extractors to such a degree that no leakage of either black liquor or chlorine takes place at the bottom. At the top the material is in a spongy state which permits good mixture with steam or chlorine. At intervals there are windows in the towers to allow the operator to see whether the reactions are taking place properly.

In the digestion process the alkali is mixed with the raw material before it enters the tower; after it passes out it is washed, pressed, and opened up before going to the chlorinating tower. The chlorine is fed in continuously at a few inches of water pressure and is so rapidly and completely absorbed that no odor is observable at either top or bottom of the tower. Prompt discharge of the chlorinated material into running cold water affords complete protection against the oxidation and hydrolysis of the cellulose which would otherwise take place as soon as the last non-cellulose portions had been chlorinated.

In present plants the operations are fully continuous. The towers each produce 8 to 12 tons of cellulose in 24 hours, but larger ones may easily be installed. One of a capacity of 1 ton per hour is comparable in size to one of the large digesters of the sulfite process.

1. Chlorine gas
2. Caustic soda
3. Cyclone
4. Screw conveyor and mixer
5. Digesting tower
6. Extractor
7. Screw conveyor and washer
8. Screw press
9. Loosening drum
10. Screw conveyor
11. Fan
12. Chlorinating tower
13. Acid pulp tank
14. Thickener
15. Alkaline washing
16. Diluting tank
17. Pump
18. Knotter
19. Sand trap
20. Strainers
21. Bleacher
22. Press - pate
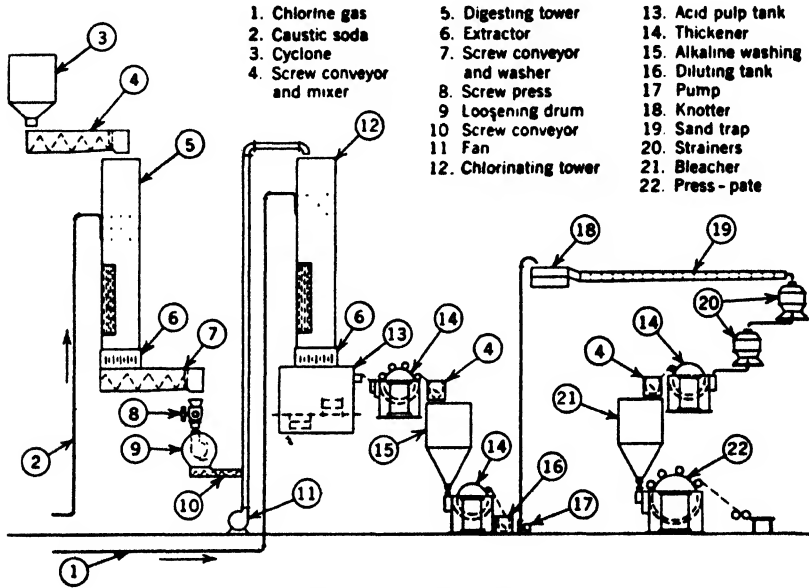
Courtesy of Paper Makers' Association of Great Britain and Ireland

FIG. 37. DIAGRAM OF POMILIO PROCESS.

Because of the dilution of the waste liquors there is no economic advantage in recovery. The mixed waste liquors are neutral, odorless, sterile, and non-fermentable, and so do not endanger animal or vegetable life, but they do have a considerable oxygen-consuming power. Representative waste liquors from a plant operating on straw had, in part, the following composition:[37]

	PARTS PER 100,000
Soluble solids	165.6
Mineral solids	62.0
Organic solids	103.6
NaCl	67.6
B.O.D. (5 days at 18.3° C.)	51.0
pH	7.1

Yields by this process have been as high as 95 per cent of the cellulose theoretically available in the raw material. Those from esparto,

straw, and similar materials are higher than by other processes because
pentosans are less attacked, as is shown by the following analyses of
esparto pulp:[20]

	ITALIAN CHLORINATION	ENGLISH SODA
Pentosans	20.0	14.6
Alpha-cellulose	78.8	72.7
Beta-cellulose	13.9	21.5
Gamma-cellulose	7.3	5.8

Table 43 shows the quantities required when treating various raw
materials, and the yields by the Pomilio process.[37]

TABLE 43

Material	Required for 100 Kg. of Air-Dry Bleached Pulp		Yield of bleached pulp
	Salt	Kw-hr. for Electrolysis	
South African wheat straw	32.1	57.8	42
German wheat straw	47.1	84.8	45
Brazilian rice straw	33.1–38.3	59.6–68.9	36–41
Lybian esparto	35.0–42.2	63.0–75 9	42–46
Java bagasse	36.7	66.1	45.2
Kenya bamboo	40.	72	50.0
Cotton linters	9.6	17.3	82
Italian spruce wood	69	122.4	46
Italian pine wood	76	136.8	43
Chestnut wood	99.8	179.6	40

The qualities of pulps made by this process differ from those pro-
duced by any other process from the same raw materials; thus soda
straw imparts wetness, transparency, and rattle, while chlorinated
straw has greater bulk and more freeness.

The Nitric Acid Process. The use of nitric acid as a pulping agent
was known as early as 1861, when Barré and Blondel took out a
patent[8] which included soaking fine pieces of wood in 36° Bé. acid for
24 hours in the cold, dilution with a large amount of water, and heating.
The pulp was finally treated with alkali and washed. More recent
experiments with the process have been along the lines of reducing the
amount or strength of the acid and cutting down the time of soaking,
either with or without the application of heat. A very complete review
of the extensive work with this process has been published by Aronovsky
and his associates.[6]

The process has attracted attention as a means of treating agricultural wastes as well as woods, and of producing pulps for both dissolving purposes and paper making.   It can be adapted to any of these products, but it has not made any headway in America, perhaps because of the disadvantages involved.   These include finer subdivision of the raw material than in other processes; a two-stage pulping process — nitric acid followed by caustic soda; the use of large amounts of nitric acid, and the need for acid-proof equipment.   To offset these in part is the possibility of using open tanks because no pressure cooking is necessary. The disadvantages are not insurmountable and may have been overcome sufficiently to justify a commercial unit of 40 tons daily capacity which was said to be established in Germany in 1936.[24]

As representative of the application of this process to annual crops, such as straw, cornstalks, and bagasse, the work of Lynch and Goss[31] may be considered.   They found that if bagasse was steeped for 3 hours in a 5 per cent solution of nitric acid at room temperatures, drained, heated for 1 hour at 80° C., washed, and boiled in a 2 per cent solution of caustic soda for 30 to 45 minutes, good yields of soft, easily bleachable fiber were obtained.   If this pulp is treated with 9 per cent NaOH solution at 100° C. the chemical constants of the pulp are distinctly altered, as is seen from Table 44.

TABLE 44

	Bleached Pulp	NaOH-Treated Bleached Pulp
Moisture...	3.9 - 6.8	4.0 - 6.5
Ash...	0.25- 0.45	0.12- 0.26
Alpha-cellulose..	86.1 -93.5	93.0 -97.4
Soda soluble (7.14% solution)........................	16 -31	5.3 -11.5
Pentosans..	9.43-11.00	2.41- 3.11
Yields (bone-dry basis)..............................	38 -40	32 -33

With such material as bagasse, 5 to 6 parts of 5 per cent nitric acid are sufficient for the first step and 70 to 75 per cent of the solution is recovered by draining.   This recovered acid can be used over and over and the same yields and quality of pulp obtained.

Further work on bagasse by Aronovsky and Lynch[5] proved that nitric acid dissolved in alcohol had much less destructive action on the carbohydrate constituents and the yields were much larger than with aqueous acid.   The yields decreased with increase in the concen-

tration of the acid or its time of action, and in the concentration of alkali or the time of treatment with it. Under similar conditions the alcoholic acid gave about 1.4 to 1.5 times the yield with aqueous acid.

The application of the process to woods has been studied by a number of workers, especially as used with German red beach. Schaarschmidt and Nowak[47] found that when red beech chips were digested for 1 hour at 100° C. with 8 per cent nitric acid solution (equal weights of wood and HNO_3) a yellowish white cellulose was obtained, which could be bleached easily after heating with a 1 per cent solution of caustic soda. Half of the acid used remained in the liquor after the digestion.

The action of 7 per cent acid on beech wood proceeds about as follows: After a short time in the cold the wood turns reddish brown and the acid becomes light yellow. No further visible change takes place in the cold, but on heating to 100° C. the reaction becomes violent and considerable quantities of gas are evolved. After about 3 hours, gas evolution stops. The undissolved residue amounts to 43 to 48 per cent of the wood used, and if sufficient acid was used the fiber can be completely freed from lignin by a short treatment with hot 1 per cent NaOH solution. It has a low copper number and a high alpha-cellulose content.

The residual acid is red or yellow according to the amount of HNO_3 used, and contains oxalic acid, acetic acid, and other by-products of the wood.

They found that, if the acid treatment was made in one step and nitric oxide was recovered, the HNO_3 necessary was about 25 per cent of the weight of the wood, but if the acid treatment was made in two steps and the recovery included hydrocyanic acid and ammonia as well as nitric oxide the acid necessary could be reduced to 15 or possibly 12 per cent. Apparently only the lignin substances are oxidized; the pentosans are partially hydrolyzed, but not oxidized.

Using aspen, Aronovsky and Gortner[2] found that alcoholic HNO_3 gave about 1.7 times the fiber yield obtained with aqueous acid and nitric oxide fumes were not given off. When 42.4 per cent of HNO_3 on the oven-dry wood was added, that used up was 9.0 to 18.8 per cent, according to cooking conditions. The yields from chips were higher than from sawdust, the figures for screened fiber being as follows:

	PER CENT YIELD FROM	
	CHIPS	SAWDUST
Alcoholic acid	41.6–45.1	30.8–39.6
Aqueous acid	28.9–31.4	25.0–28.6

From other data it is found that fiber with good paper-making characteristics can be made from poplar, beech, birch, maple, spruce, and western hemlock. Poplar can be reduced with weaker acid than the others, but the actual consumption of HNO_3 is about the same as for the other hardwoods. For well-reduced pulp 18 to 20 per cent of HNO_3 on the bone-dry wood is a fair estimate, while for an inferior, undercooked pulp 14 per cent is about the minimum. As compared with this the amount which has to be used is much greater because of the necessity for saturating the chips with a relatively dilute acid — about 7 to 10 per cent strength. About 65 per cent of the original volume used can be recovered, but it contains only about 65 per cent of its original HNO_3. Contrary to the results of Lynch and Goss the re-use of recovered acid gave lower yields and darker-colored fiber.

Pulp overtreated by this process is greenish or yellowish in color and darkens on exposure to light, even when kept in a closed jar. The fibers are broken and cracked in many places, show a strong oxycellulose reaction, and gelatinize in the presence of alkali. Well-made pulp, however, is characterized by a low copper number and a low ash and high alpha-cellulose content. From the paper-making standpoint it has interesting properties, somewhat resembling the purified high-alpha pulps. When made from poplar it shows more resistance to long beating than soda poplar fiber and the beaten pulps are freer and have greater tearing, burst, and folding strengths and less shrinkage. The sheets have a desirable softness, somewhat resembling that of rag papers.

The future of this process is difficult to predict. It has possibilities from the standpoint of both paper-making and cellulose-dissolving industries, but whether the fiber can be made at a price to compete with other processes depends on the cost of nitric acid, the installation cost, and the questions of recovery and re-use of acid and the preparation of by-products. Under present conditions it does not appear to be very attractive to the paper maker.

Organic Reagents. Processes employing organic reagents, especially the aliphatic mono- and polyhydroxy alcohols, have been used in recent years for isolating lignin in order to study its properties, and Phillips[36] cites a considerable number of references on the subject.

Among the earlier references to such agents is the process of Engel and Wedekind,[23] who found that the incrusting materials of plant substances could be brought into colloidal solution by heating for several hours at about 90° C. with dioxane, which is a cyclic diether and contains no chemically reactive groups. For example, if spruce chips are treated with eight times their weight of dioxane for 5–10 hours at

80–90° C., and with a small addition of hydrochloric acid, the residual cellulose can be easily washed with water and the yield of pulp is about 60 per cent.

More recently Aronovsky and Gortner[3] have reported on experiments using various organic reagents. Their cooks were made in a small autoclave using 100 grams of sawdust and 1500 cc. of a mixture of equal volumes of water and the liquid reagents or 1500 cc. of water in which the solid reagents were dissolved. The pressure employed was 150 pounds, and temperatures ranged from 157 to 186° C.; about 1 to 1.5 hours was required to reach pressure, which was then held for 4 hours, after which it was relieved to atmospheric pressure. They found that alcohol-water ratios of 1 : 1 and 6 : 4 were suitable for pulping but that higher concentration decreased the pulping effect.

Table 45 shows the results obtained when cooking aspen sawdust. The yields of residual wood are those after extracting the cooked mass with benzene-alcohol. As noted above, water was used with all the reagents mentioned in the table.

TABLE 45

Cooking Agent	Residual Wood	Cooking Agent	Residual Wood
Water only	63.4	tert-Amyl alcohol	60.2
Methyl alcohol	70.2	Dioxane	63.4
Ethyl alcohol	62.5	Ethylene glycol	53.2
n-Propyl alcohol	60.0	Glycerol	54.9
Isopropyl alcohol	66.1	d-Glucose (40%)	67.9
n-Butyl alcohol	54.1	d-Mannitol (40%)	58.1
Isobutyl alcohol	57.1	Urea (40%)	78.6
tert-Butyl alcohol	68.1	n-Butyl alcohol 20% urea	74.3
n-Amyl alcohol	51.5	n-Butyl alcohol 10% urea	68.1
Isoamyl alcohol	52.6	n-Butyl alcohol 5% urea	66.2

Of the residual woods those from n-butyl alcohol, n-amyl alcohol, ethylene glycol, and glycerol were semi-pulped; the others were soft or pliant and of various shades of brown. Of the polyhydroxy alcohols the best pulping agent seems to be ethylene glycol, while the n-butyl alcohol-water mixture is the most efficient in removing lignin. The extracted lignin is probably less changed in character than that removed by the usual cooking processes. The pulping ability of the alcohols increases as the straight-chain length of carbon atoms increases. Apparently an alcohol must have at least four carbon atoms, three of which are in a straight chain, in order to produce a well-pulped residue. The more insoluble alcohols are the best pulping agents.

In addition to the work on sawdust this paper also gives the details of cooks of aspen chips with water-*n*-butyl alcohol mixtures. The yields were from 47.0 to 56.5 per cent of screened fiber with an alpha-cellulose content varying from 72.0 to 85.6 per cent, and the maximum screenings in any cook were 4.0 per cent. These pulps were said to have bursting strength and tearing resistance characteristics similar to those of commercial alkaline aspen pulps, but were softer and more absorbent and seemed to hydrate faster on beating.

Cooks of jack pine indicated that different digesting conditions would be necessary for this wood, and work by McMillen, Gortner, Schmitz, and Bailey[35] indicated that hardwoods were distinctly different from softwoods. Their work also was done on sawdust, and for 100 grams of wood they used 800 cc. of water and 800 cc. of technical *n*-butyl alcohol. They digested for 6 hours at 158° C. (151 pounds pressure), cooled without relief to 60° C., placed the contents on a Büchner funnel, and gave it a series of washings which included *n*-butanol, dilute alkali, water, dilute acid, water, very dilute ammonia, and water. The yields obtained by this procedure are shown in Table 46.

TABLE 46

Hardwoods	Yields	Softwoods	Yields
Aspen	54.2	Jack pine	59.5
Silver maple	46.3	Red pine	58.3
Basswood	43.6*	Tamarack	57.2
White oak	43.1	White spruce	60.0
Red oak	45.4	Black spruce	58.4
Paper birch	45.3	Balsam fir	68.4

*Slightly low because of a little loss of fiber

The lignin contents of the original wood and residual pulp were found to be:

	ORIGINAL WOOD	RESIDUAL PULPS Based on pulp	RESIDUAL PULPS Based on wood
Lignin in hardwoods	16.7–22.2	3.4– 4.9	1.6– 2.6
Lignin in softwoods	25.1–28.4	17.2–22.9	10.0–15.7

The alpha-cellulose in the residual pulps ranged from 75.1 to 79.0 for the hardwoods and from 56.0 to 67.1 for the softwoods. All the hardwoods yield pulps which, according to their chemical analyses, would be satisfactory commercial products, but no tests of their paper-making value were made.

Later work by Bailey[7] has confirmed the difference between aspen and jack pine when treated with butanol and has shown that if the butanol is rendered 2 per cent alkaline by NaOH all the lignin can be removed from the pine. The alkali functions chiefly as a catalyst.

Working with western hemlock and white fir sawdust, Friedman and McCully[25] found that lignin could be almost completely extracted by benzyl alcohol. They extracted the dried sawdust first for 10 hours with alcohol-benzene mixture, pressed out the excess of the mixture, oven-dried, extracted 10 hours with water, dried, and finally extracted 1 hour at 105° C. with pure benzyl alcohol containing 3 per cent of HCl.

From the very meager information available it would seem that satisfactory paper pulps can be made by digestion with several of these reagents, at least from hardwoods, but such processes do not appear to have any advantages which would warrant their employment unless some profitable use can be found for the lignin and other materials dissolved during the digestion.

Neutral Sulfite Processes. The use of acid sodium sulfite for pulping is mentioned as early as 1871, and by 1880 Cross had brought out a process using alkaline solutions of sulfite in iron digesters.[27] In 1901 Schacht took out patents[48] for preparing cooking liquor by treating a solution of crude recovered soda with SO_2 until it was nearly saturated, and then causticizing the residual carbonate. This liquor contained Na_2SO_3, $Na_2S_2O_3$, and NaOH, the last only in the amount considered necessary to deal with the silicates and aluminates of the raw materials.

Drewsen[21] used sodium sulfite in the absence of any substantial amount of alkali for pulping corn stalks, bagasse, and similar materials and recognized the necessity for maintaining slightly alkaline conditions throughout the cook. Braun[11] took out a patent covering the use of Na_2SO_3 and Na_2S alone or in conjunction with the Na_2CO_3 and an alkaline soap, and in later patents[12] proposed the use of some NaOH with the sulfite and sulfide, and the use of alkali silicates and sulfites, with or without the addition of caustic alkalies, alkali carbonates, or monosulfides.

Apparently nothing radically new was involved in the so-called " Keebra " process,[1] which started by using neutral sodium sulfite for cooking hardwoods, or sulfite containing more or less caustic soda for resinous softwoods. Later this was broadened to include additions of other substances such as $NaHSO_4$, Na_2S, $Na_2S_2O_3$, Na_2CO_3, $NaHCO_3$, Na_2SO_4, and NaCl, and each of these was given a distinctive name.[10] Apparently these were more or less speculative in nature, and so far

as is known the only one which has survived is that which uses Na_2CO_3 or $NaHCO_3$ with the Na_2SO_3.

The semi-Keebra process, using some NaOH with the Na_2SO_3, was used in one mill from 1922 to 1930, but was then discontinued. During its use the amount of Na_2SO_3 was started at about 15 per cent (based on Na_2O) and gradually reduced to 6 per cent. The fiber was considered equivalent to soda fiber, and the advantage of the process was an increase in yield of about 5 to 10 per cent. The chief objections were the corrosion of the evaporators and rotary furnaces in the recovery department, and the occasional bad odors if the burning of the liquor was not carefully conducted.

At present the neutral sulfite process is being used in one mill which produces about 10–15 tons of fiber per day by this method. The modification used is patented[50] and is called the " sodite " process. It employs Na_2SO_3 accompanied by definite amounts of Na_2CO_3 and can be applied to all softwoods which have been tried, regardless of the resin content. The pulp bleaches more readily than sulfate pulp but otherwise is very much like it in paper-making value, though some of the chemical constants differ considerably, and it would seem that the sodite pulp should be the more permanent of the two. When applied to hardwoods the difference between the sodite and the usual alkaline processes is more marked. The sodite process gives a radically higher yield — as much as 50 per cent for softwoods and 60 per cent for hardwoods on the bone-dry basis — and a much stronger and whiter pulp than can be obtained by the alkaline processes. The process may be applied to mixed woods, as pine and poplar, or tamarack and birch; the longer time necessary does not seem to injure the fiber from the wood which cooks the more easily.

As described in the patent specifications the actual analyses of two composite samples of cooking liquor were:

	POUNDS PER CUBIC FOOT	
	1	2
Sodium bicarbonate	0.79	0.92
Sodium sulfite	12.40	12.70
Sodium thiosulfate	2.08	0.98
Sodium sulfate	1.07	1.00

The normal impurities as shown in these analyses do not harm the pulp.

A comparison of the preferred cooking conditions for softwood and hardwood follows:

	SOFTWOODS	HARDWOODS
Cubic feet of cooking liquor per cubic foot of chips	0.25– 0.75	0.25– 0.75
Na_2SO_3, per cent on bone-dry wood ...	40 – 45	30 – 40
$NaHCO_3$, per cent on bone-dry wood ..	1.5 – 3.0	1.3 – 2.6
Temperatures in digesters, °C.	175 –188	175 –188
Time to reach pressure, hours	2 – 3	1 – 2
Total time, hours	6 – 12	3 – 7

The pH of the cooking liquor is about 7.5–9.5; during the first part of the cook it drops and then rises again, but never goes substantially below 7.0. The pH in the recovered black liquor, 8.5–10.5, is caused by the breaking up of $NaHCO_3$ on heating and the escape of CO_2 and also by the neutralization of organic acids by the Na_2CO_3. The presence of the Na_2CO_3 in the liquor is essential to guard against excessive corrosion, and if desired it may be added as such to the cooking liquor; ordinarily $NaHCO_3$ is unavoidably present if the cooking liquor is made in the usual way by passing SO_2 into the recovered alkali. Experience has shown that even under the best conditions the liquors are much more corrosive than the alkaline liquors of the soda and sulfate processes, and lined digesters should be used.

If the cooking liquor needs dilution, black liquor may be used safely, as it causes no injury to the fiber and supplies considerable of the necessary chemicals. The Na_2SO_3 must not be entirely used up during the cook; if this happens the thiosulfates present as impurities cause the pulp to become brown or black. It is also necessary to avoid high alkalinity in the presence of black liquor as this seems to set the color on the fiber with decidedly harmful results.

The alkali from sodite black liquor is recovered by evaporation and incineration, and a final treatment with SO_2. When concentration is performed in multiple-effect evaporators, deposition of organic matter on the tube walls causes trouble which may be avoided by adding NaOH to the liquor before evaporation. This holds the organic matter in solution and supplies the alkali necessary to make up for the unavoidable losses in the cooking cycle. If it is available, soda-process black liquor may be used for this purpose.

The ash from the incinerators contains chiefly carbon and Na_2CO_3, or if smelters are used it forms a molten mass practically free from carbon. Under ideal conditions all the sulfur would be burned out, but this is neither practicable nor necessary. The final step, treatment with SO_2, causes the formation of Na_2SO_3 and of $NaHCO_3$ from the Na_2CO_3. If Na_2S is present this is converted to $Na_2S_2O_3$, which is undesirable; this can be avoided by first treating the liquor with CO_2, but

a considerable excess is needed to sweep out the H_2S, and it is better to pass both SO_2 and CO_2 through at the same time, the CO_2 being in considerable excess so that practically all the SO_2 is absorbed. When the remaining $NaHCO_3$ reaches the desired concentration the action is stopped and the liquor is ready for use.

This process fits in best in a mill making sulfate pulp as this permits recovered liquors to be used to the best advantage and avoids awkward recovery steps. Difficulties connected with efficient alkali recovery have probably kept this process from making the headway which the quality of the fiber seems to warrant.

Clark,[16] reporting on the working of the Keebra process in a Canadian mill, found that pulp cooked with Na_2SO_3 alone was harder, stronger, and more transparent than regular soda pulps, but that the difference was less apparent when part of the alkali consisted of NaOH. The color of unbleached Keebra pulp from spruce or hemlock approached that of unbleached sulfite, while poplar pulp had a color comparing favorably with fairly well-bleached pulp.

Rawling and Staidl[38] used Na_2SO_3 and finely divided aspen wood, and found that when the cook was made at 170° C. for 4 hours the yield was practically constant even when the Na_2SO_3 varied from 12 to 120 per cent of the wood. They also found that with constant Na_2SO_3 at 50–54 per cent of the wood the yield of total fiber dropped consistently with increasing temperature between 120° and 185° C. The removal of other substances than lignin required a temperature over 170° C., though this takes place below 140° C. in caustic soda cooks.

Bray and Eastwood[13] find that the yield decreases with the time of cooking with the neutral reagents, regardless of the ratio of the two chemicals. Substitution of bicarbonate for part of the sulfite increases the rate of reaction during the first 2 hours, or until the concentration of sulfite has reached approximately 8–10 grams per liter. Beyond this point larger yields were obtained by replacement of the sulfite by bicarbonate. Cooking liquor containing sulfite alone seems to attack the alpha-cellulose more than when bicarbonate is present. The rate of lignin removal was greatest during the first 2 hours and decreased as Na_2SO_3 was replaced by $NaHCO_3$.

Later studies by Chidester and McGovern[15] were made on shortleaf pine chips with the addition of NaOH, Na_2S, or $NaHCO_3$ to the Na_2SO_3 cooking liquor. The initial pH values were 8.10 for Na_2SO_3 alone, 9.05 and 11.0 for two cooks containing NaOH, 9.15 and 11.1 for two with Na_2S added, and 8.2 for one with $NaHCO_3$. The cooks were made at 138 grams per liter of Na_2SO_3, and the temperature was brought to 180° C. in 3 hours and held there for $6\frac{1}{2}$ hours. All yields were rela-

tively low — 40.8 to 44.2 per cent of screened pulp — but the highest were from the cooks with caustic soda added and the lowest from that with bicarbonate. The bleach required was about 25 per cent for pulps from cooks with Na_2S added and from 31 to 35 per cent for the others. All the strength values were relatively high compared with sulfite or sulfate pulps from the same woods.

Similar work on other woods gave even better results with some of the finer-fibered softwoods, while some of the hardwoods, notably yellow birch, gave pulps with bursting strengths not far below those of an average kraft pulp from pine.

Aronovsky and Gortner[4] cooked aspen sawdust with 23.8 and 47.6 per cent of Na_2SO_3 on the bone-dry wood, and at temperatures of 170° and 186° C. for 2 and 12 hours. In apparent contradiction to Rawling and Staidl they found that higher percentages of sulfite gave lower yields. If the conditions were severe enough the wood was fully pulped, but the yields were low. Detailed studies of the distribution of the various constituents of the wood in the liquor and the residual wood led them to conclude that Na_2SO_3 hindered the destruction of the alpha-cellulose at higher temperatures and longer times of cooking.

Semi-Chemical Processes. The basic principle on which these methods depends is digestion under relatively mild conditions, which soften but do not fully pulp the chips, and their subsequent reduction to pulp by some form of mechanical disintegration. There is nothing new about such ideas, and many schemes have been proposed, but except for the production of steamed groundwood none had been extensively employed until about 1926. Unfortunately the name " semi-chemical " has been rather generally assumed to apply only to those cooks in which the chemical used was neutral sulfite of soda; actually there are a number of other processes operating under acid or alkaline conditions which are equally deserving of the name. These include the semi-sulfite, semi-sulfate, the polysulfide process, and others.

Neutral Sulfite. This name also is not entirely descriptive, for it is recognized that digestion must be carried out under slightly alkaline conditions, but as the active pulping agent is Na_2SO_3 the name is perhaps justified.

The process as originally described[44] consists in: (1) a preliminary impregnation of the chips with the cooking liquor; (2) a mild digestion with chemicals which are practically neutral and capable of maintaining neutrality in spite of the liberation of organic acids from the wood; and (3) a mechanical reduction of the softened chips.

The chips are charged into digesters, preferably globe rotaries, and steamed for half an hour at atmospheric pressure, and the digester is

then filled with liquor, which is forced into the wood at a pressure of about 100 pounds per square inch to insure uniform distribution of the cooking chemicals throughout the chips. The unabsorbed liquid is blown back to the supply tank to be adjusted for further use. The impregnation should be completed at a temperature of 120° to 125° C., since most of the organic acids are set free at 110° to 130° C., and it is advantageous to cause their liberation while the digester is full of liquor in order to prevent its corrosion by acid vapors. After the excess liquor is blown out the charge is brought to a temperature of 140° to 160° C. and held there for 4 to 6 hours. Higher temperatures or longer time lowers the yield. Rotation of the digester or circulation of the liquor is essential to uniform digestion.

The total quantity of chemicals used in this process need not exceed 15 pounds per 100 pounds of wood, but the $NaHCO_3$ must be sufficient to neutralize the acids formed. Sodium carbonate, or even caustic soda, may be substituted for the bicarbonate, but the pulp will then be darker in color.

At the completion of the digestion period the chips are not reduced to pulp but retain a considerable part of their rigidity. They are dumped, washed, and reduced to pulp by mechanical means, as by a rod mill, after which the pulp is sufficiently like chemical pulp to be washed, screened, and handled in the usual way. The yields obtained from hardwoods by this process range from 70 to 85 per cent on the oven-dry basis; those from conifers are slightly less.

The process seems to be especially adapted to the decidous woods, and the pulps have strength and flexibility far in excess of soda pulps from the same woods. Conifers yield readily to the treatment, but the pulps are weaker and less flexible than would be expected from their fiber length. The pulps from deciduous woods can be used in newsprint as a partial or full substitute for sulfite. For boards, darker-colored woods or more alkaline liquors may be used; the first commercial application of the process was for the production of corrugated board from chestnut chips in 1926.

According to Curran,[18] the most serious obstacle to the general use of this process is the color of the pulp. Since no satisfactory method of bleaching it is yet known, its color depends largely on that of the original wood, but may be influenced to some extent by the cooking conditions employed. The quality of the product will vary according to the treatment, and in laboratory operations has ranged from the crudest board to light-colored print and catalog papers, and from sheets so weak as to be practically valueless to those strong enough for wrapping papers.

Ammonium sulfite. More or less work has been done with this as a cooking agent, and the process prior to 1925 has been reviewed by Rue.[43] The treatments proposed have included use of the neutral salt; the addition of an excess of ammonia[14] to permit the use of lower temperature and neutralize acids formed from the wood; the use of ammonium bisulfite, with or without sulfurous acid or a soluble sulfite;[33] and the use of ammonia gas and sulfur dioxide, followed by a mild mechanical disintegration.[46] Some of these processes are said to give good yields of easily bleachable pulp, while others yield impure products of the " semi-cellulose " grade.

A more recent laboratory study of this pulping agent has been made by Hepher and Jahn[28] using crystallized ammonium sulfite and working with both sawdust and chips from lowland fir (*Abies grandis*). Chips gave a yield of about 73 per cent when using 25 per cent of chemical, impregnating for about $2\frac{1}{2}$ hours at 127° C., and cooking for about $3\frac{1}{2}$ hours at 175° C. The pulp was coarse, but would be suitable for boards or coarse papers. Practically the same yield of a better product was obtained when 35 per cent of chemical was used. Both products had to be disintegrated mechanically.

From the cooks of sawdust it was found that the lignin removal increased with increase in (a) the amount of chemical, (b) the length of the digestion, and (c) the temperature employed. The cellulose content of the residual wood increases as the chemical used rises to 50 per cent of the dry wood, and then decreases. Since ammonium sulfite in solution hydrolyzes and reacts alkaline, addition of either ammonia or sulfur dioxide would be expected to alter the action on the wood. This was found to be true; adding ammonia increased the yield and the pentosan removal and decreased the degradation of the cellulose, while the reverse was true if sulfurous acid was added. The yield decreased with increasing temperature or duration of cook, but varied comparatively little with increased amounts of chemical.

Semi-Sulfite Process. This process has been described in two papers by members of the Forest Products Laboratory.[19,29] It employs the usual bisulfite cooking liquor, but conditions are so regulated that the chips are thoroughly penetrated at or below 110° C. This is followed by a mild cook at a lower temperature, lower concentration of chemical, lower ratio of chemical to wood, a shorter time than usual, or any combination of these conditions. The most important step is the penetration period, which should be prolonged rather than shortened, in order to obtain uniformly softened material. The chips, which retain their original form, are blown from the digester, thoroughly washed, and then mechanically disintegrated. Yields of 63 to 75 per cent on the

bone-dry basis can be obtained from white spruce, while hemlock, jack pine, or loblolly pine will yield from 56 to 73 per cent. If the yield is above 60 to 65 per cent difficulty may be expected in discharging the contents of the digester. The additional cost of rod milling to reduce the chips to pulp seems to be more than saved by the increase yield.

The product can be used in place of sulfite in the production of newsprint. As compared with stock containing ordinary sulfite that with semi-chemical pulp develops burst and tensile strength more easily and to a higher degree; tearing strength is likely to be lower, folding about the same, and freeness and porosity lower. The paper produced is harder, stiffer, takes a higher finish, and is less permanent. The color is not much different at first, but it degrades more rapidly than when quick-cook sulfite is used.

The Polysulfide Process. This process was advocated by Drewsen,[22] who patented the cooking of chips with calcium polysulfide containing a high proportion of lime. After cooking, the chips were crushed and boiled with soda ash solution to remove all sulfur. The process was designed to produce bleachable fiber, but the dark-colored intermediate product was considered usable for wrapping papers. Apparently the pulp remained harsh and woody even after beating.

Tingle's process[51] also employed polysulfide, but the ratio of lime to wood was lower as a bleachable product was not desired. He prepared the polysulfide separately by heating sulfur, lime, and water under moderate pressure and settled out the impurities. Enough of the liquor was employed to correspond to 6.66 per cent of sulfur and 13.3 per cent of quicklime, based on the air-dry wood, and the digestion time was 10 to 12 hours at 65 to 75 pounds pressure. At the end of the digestion the liquor was dark colored and had an offensive odor; the chips were brown and retained their original form, though they were more easy to disintegrate than before treatment.

These cooked chips were then subjected to a second treatment with a reagent capable of removing calcium compounds; dilute sulfuric acid, oxalic acid, and fresh waste sulfite liquor were mentioned as suitable. The action should be aided by crushing the material with blunt knives in the beater or in an edge runner, and after reducing to the desired degree the pulp may be washed and screened as usual.

This pulp was said to be of different shades of brown according to the degree of treatment. Yields of approximately 70 per cent were obtained, and the remaining lignin was considered much more stable than usual because exposure to direct sunlight for 3 months caused no deterioration. When skillfully handled in the beater it was said to

give very strong paper. So far as is known this process has never been used commercially.

Ramar Process. This semi-chemical process, which is covered by a series of patents,[32] consists in digesting the wood with solutions of neutral chemicals which convert the intercellular binding material into a readily friable but insoluble condition. The chemicals which are said to be able to accomplish this include chlorides or nitrates of the alkali or alkaline-earth metals, and sulfates of sodium, potassium, magnesium, aluminum, copper, iron, and manganese, with or without the addition of a long list of other salts. After digestion the wood is crushed, shredded, and placed in a beater where the finely divided binding material may be washed out with an ordinary washing drum. It is claimed that yields of 85 to 95 per cent are obtained according to whether the friable material is washed out or remains with the fiber. The product is said to make an exceptionally strong paper.

Lime Cooking. According to Sokolovskii,[49] a good grade of wrapping paper can be made from birch wood by cooking with 2° to 2.5° Bé. calcium hydroxide for 6.5 hours at 150° C. and a pressure of 5 atmospheres. With aspen wood, 2° Bé. lime and 4 hours' cooking are sufficient, and a yield of 91.5 per cent of half stuff was obtained. The material is not suitable for bleaching.

The Explosion Process. This process for the production of wood pulp was devised by W. H. Mason[34] largely as a means for utilizing wood waste, but later the supply of such material became exhausted and cord wood is now being purchased and used.

The wood is hogged or chipped to about the size used in ordinary pulp production, and sawdust is removed by screening. The chips are then charged into vessels in which they are steamed under high pressure and then suddenly discharged to atmospheric pressure. The "guns" used for this work are about 20 inches in diameter and 5 feet high, with a capacity of about 10 cubic feet.[9] They consist of vertical cylindrical chambers, fitted with a chip inlet at the top and a discharge valve at the bottom. The inlet is closed by a taper valve, and the bottom outlet is preferably slot-shaped, of uniform width and tapered at the sides, gradually expanding outwardly. Pipes are also supplied for the introduction of steam, compressed air, water, or other fluids as desired.

In operation, about 200 pounds of chips are placed in a gun and steam is turned on to bring the chips to about 375° F. During this time the condensate is continuously removed by an automatic trap. After holding at this temperature for 30 to 40 seconds, high-pressure steam is admitted and 1000 pounds per square inch, equivalent to a temperature of 540° F., is reached in 2 to 3 seconds. After 5 seconds

the hydraulic discharge valve is opened and the chips pass through a small port in the bottom, where they explode immediately. Compression of the chips in passing the restricted opening appears to aid in their disintegration, and the steam pressure is kept turned on during the discharge so that all chips are disintegrated to the same extent. It has been found that if the wood is discharged at a pressure of less than 275 pounds nothing more than a partial shredding is accomplished, but at high pressure the disintegration is practically complete. The discharge from the guns passes to a cyclone separator to separate steam and fibers. Hot water is added and the stock kept at 160° F. while being refined in rod mills. It is then screened and passes through conical refiners similar to jordans, except that the stock enters at the large end. The stock from the guns has a pH of about 4.5 while that from the last refining process should be at about 6.5.

The wood used in this process has been largely pine, but hardwoods are being used in increasing amounts. It has been found that very dry wood requires less time for preheating than green wood, and the timing must be very closely watched in order to avoid raw or burned " shots." Bark entering the guns is completely pulverized and is said to be carried off in suspension with the white water. The latter is clarified and re-used in order to save heat and dissolved solids.

Chemically this process involves acid hydrolysis which converts certain portions of the wood into soluble substances, largely sugars and acids. The sugars include the pentoses, xylose and arabinose, and the hexoses, glucose, mannose, and galactose. The acids are chiefly acetic and formic, but some higher acids are also present. These water-soluble substances must be washed out of the pulp if satisfactory boards are to be made. Formerly they constituted a stream-pollution nuisance, but more recently recovery methods indicate that useful products can be made from them.

Fiber produced by this process is usually darkened somewhat by the treatment. It has not found any appreciable use in paper making, but it serves excellently for the manufacture of insulating board because the bundles of fibers give the loose, puffy structure necessary for this class of material. A board of unusual hardness, density, and stiffness can also be made from it by forming the boards on a Fourdrinier and drying them in hydraulic presses with steam-heated platens. Under these conditions the lignin, or other incrusting substances, which were first softened to permit the wood to be disintegrated, are again softened by the heat in the presses and on drying out act as binding agents. This type of board is claimed to expand and contract with changing humidity conditions far less than wood.

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CHAPTER IX

BLEACHING

John D. Rue

None of the commercial methods for isolating paper-making celluloses produces perfectly pure material, as small amounts of non-cellulose matter in the raw materials escape destruction during the processes, and other impurities may be formed by them. Bleaching is therefore necessary to brighten and whiten the product and incidentally to purify it by removing both colored and colorless materials. The degree of purification is closely related to the brightness attained and the permanence of the bleached product. Some grades of pulp are used almost entirely without bleaching, but most are bleached to some degree.

Evaluation of Bleaching Results. The bleaching procedure followed depends on the process used in isolating the fibers and on the properties desired in the bleached product, and its success is judged by the degree to which the product meets the needs of the paper maker. For control purposes it may be evaluated not only by the degree of brightness, but also by tests for strength, freeness, cleanliness, softness, opacity, absorbency, viscosity, and chemical tests.

The trade terms to denote the degree of bleaching, such as " full bleach," " semi-bleach," and " slightly bleached," are very indefinite and cause misunderstandings, but fortunately facilities are now available for measuring color and whiteness by methods which are briefly described in Chapter XV. If a single value for brightness is determined by making readings through a filter which passes light rays for nearly the entire visible spectrum the readings serve to grade pulps in nearly the same order as by visual comparison. Pulps may, however, have the same brightness values, yet appear different to the eye because of differences in the curves which the spectrophotometer would reveal.

The following table shows the approximate relation of brightness values to the common trade terms for bleached fibers:

Fiber and Trade Term	Brightness	Fiber and Trade Term	Brightness
Sulfite: full bleached ...	80–85	Sulfate: full bleached ...	75–85
semi-bleached ..	72–78	semi-bleached ..	65–70
unbleached	61–68	slightly bleached	40–50
		Soda: full bleached ...	77–82

The strength factors and the way these behave as the pulp is beaten are of prime importance in both experimental and commercial bleaching. Methods for making such tests, and also for chemical tests, will be found in Chapter XV, and the present discussion will deal with trends rather than specific data.

Purification and Bleaching Reactions. Impurities which are contained in unbleached chemical wood pulps and which must be removed, or may be removed incidentally to a considerable degree, include lignin residues, carbohydrate residues, extractives of various kinds and degrees of color, resinous materials from the inner bark or from the regions surrounding the knots, dyes such as the tannins, phlobotannins, etc.

The true bleaching reaction is chiefly one of oxidation, and oxidizing chemicals were for many years the major reagents used. In recent years, however, some of the impurities are removed with a high degree of selectivity by reactions which are applied successively. Typical examples of selective reactions are those of chlorine with lignin; of caustic soda with chlorinated residues, the non-alpha constituents of cellulose, or the brown dyes found especially in sulfate pulps; and of sulfur dioxide with ferric iron and some of the other mineral constituents of the ash. It is important that purification by one or more of these reagents precede brightening by oxidation, as the impurities are then removed with a minimum of attack on the cellulose and those portions of hemicellulose which must be retained if the pulps are to have the qualities desired in paper making.

Of the oxidizing agents the hypochlorites are most extensively used because of their low cost and generally favorable action. Chlorates react too slowly; chlorites[7,11,12] have recently attracted attention and are being tried commercially but cannot be said to have attained an established position in pulp bleaching. Permanganates give excellent results but show no superiority which justifies their greater cost.

Hydrogen peroxide has been used in the textile industries but has no recognized place in bleaching wood pulp, though it has recently been proposed[4] as a final or flash bleach for pulp in a web or sheet. Sodium peroxide hydrolyzes in water to a strongly alkaline solution of hydrogen peroxide, which reacts so vigorously that it is difficult to avoid undesirable attack on the fibers, and it has found no place in bleaching wood pulps.

Chlorine. Chlorine is used in its elemental form for direct chlorination of pulps and also to chlorinate lime milk and caustic soda solution in preparing hypochlorites for use as oxidation bleaching agents. Chemically pure and anhydrous chlorine reaches the consumer in the

liquid form under pressure in 100- and 150-pound cylinders, in 1-ton containers, and in 16- and 30-ton single unit tank cars. The pressure varies with the temperature as shown in Fig. 38. The liquid contains less than 0.2 per cent of impurities, which consist mainly of ferric chloride, hexachloroethane, carbon tetrachloride, and chloroform.
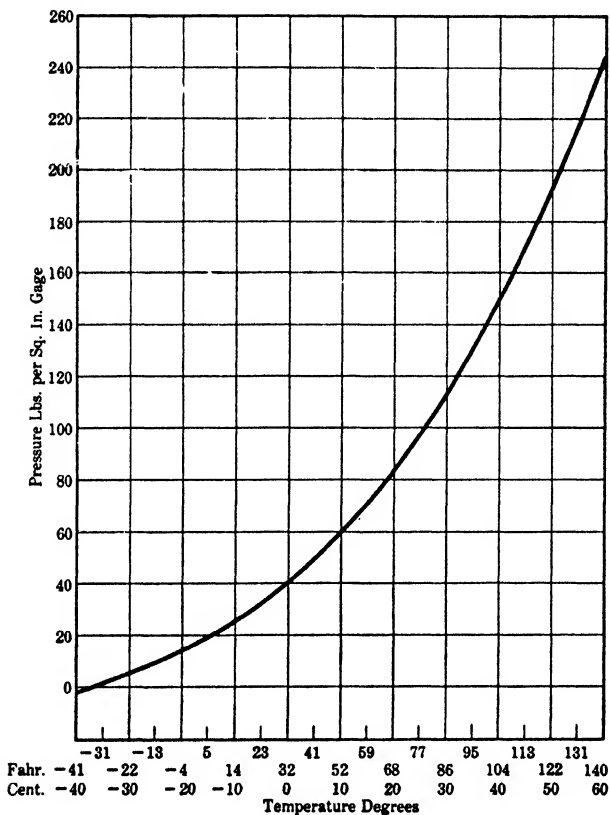
International Critical Tables.

FIG. 38. VAPOR PRESSURE OF LIQUID CHLORINE.

Some mills produce their own chlorine electrolytically, in which case it is available in the form of moist gas containing about 5 per cent or more of gaseous impurities, chiefly oxygen, nitrogen, some carbon dioxide, and a trace of hydrogen.

At normal temperature and pressure chlorine is a gas with a specific gravity of 2.49 (air = 1), but it is readily liquefied under pressure at reduced temperature, and the liquid then has a boiling point at 760 mm. pressure of –33.6° C., a freezing point of –101.5°C., and a

specific gravity of 1.47 (water = 1). One volume of the liquid yields 460 volumes of gas, or 1 pound yields 5 cubic feet.

The specific heat of the liquid is 0.2257 caloric per gram per degree centigrade, between 0 and 24° C., or 0.2257 B.t.u. per pound per degree Fahrenheit between 32° and 75° F. Its heat of vaporization is 67.1 calories per gram at –34.6° C. or 121 B.t.u. per pound at –30.3° F. It is a non-conductor of electricity. It is soluble to a limited extent in water; its solubility at three pressures and at temperatures between 10° and 100° Ċ. is shown in Fig. 39. When chlorine water is cooled to approximately 0° C., chlorine hydrate separates as pale yellow crystals ($Cl_2 \cdot 8H_2O$, according to Roozeboom), mixed with ice crystals. Chlorine hydrate forms at temperatures between 0° and 9.6° C. when chlorine is brought into contact with a limited amount of water. When chlorine is passed through a moist pipe the crystals formed may plug it up, and when bleach liquor is being made with cold water chlorine hydrate may form and be carried to the surface of the solution and there give off chlorine vapors to the warmer air.

FIG. 39.　SOLUBILITY OF CHLORINE IN WATER.

The chemical reactions of chlorine which are of interest in connection with its use in bleaching are those with the materials used in the construction of equipment and those affecting its efficient use as a chlorinating or oxidizing agent.

Chlorine is non-explosive and non-inflammable, and in the absence of moisture is very inactive and can be stored and handled in iron so long as the temperature does not exceed about 100° C. In the presence

of moisture it is exceedingly active and attacks most metals and alloys. Among the materials which have found practical application in handling chlorine in the presence of moisture are: tantalum; alloys of iron, silicon, and other ingredients; an alloy of chromium, nickel, and molybdenum; rubber (provided it is not flexed); and coatings with a base of chlorinated rubber or similar material.

When chlorine is dissolved in water the reaction may be represented as follows:

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl$$

When the pH is below 2 the equilibrium is shifted sharply to the left, but as the pH is raised by addition of an alkali it shifts toward the right, and at about pH 5 the concentration of HOCl is at a maximum. Further increase of pH may be represented by the following reaction, in which an increase in pH again shifts the equilibrium to the right:

$$HOCl + NaOH \rightleftharpoons NaOCl + H_2O$$
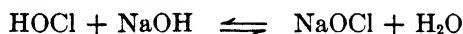
The products formed on dissolving chlorine in water depend, then, on the pH, and the changes in composition which take place with changes in pH are reversible. The following table summarizes roughly the equilibrium conditions:

Below pH 2	Chlorine present predominantly as elemental chlorine.
pH 2–3	Elemental chlorine present along with hypochlorous acid.
pH 4–6	Hypochlorous acid predominates.
pH 7–9	Hypochlorous acid present along with hypochlorite.
Above pH 9	Chlorine present predominantly as hypochlorite.

Besides these, hydrochloric acid is present, but this plays no direct part in bleaching and purification except as it may dissolve some of the mineral impurities.

Chlorine, when present chiefly as dissolved chlorine, has a strong tendency to act as a chlorinating agent with organic matter, either by addition or substitution, and such reaction will continue as long as there is material to be chlorinated. If such material is absent and appreciable quantities of HOCl are present, then the secondary tendency to oxidation will become apparent.

Hypochlorous Acid. HOCl is a weak acid, weaker even than H_2CO_3, and so can be liberated from its salts by CO_2. It is volatile with steam, and some of the chlorine from a hypochlorite solution or from a bleaching mass may be lost by volatilization of HOCl if the pH becomes too low. It is a strong oxidizing agent and reacts so vigorously and rapidly with organic matter that it is difficult to direct its action

selectively on the impurities; before they can be adequately attacked the cellulose is also attacked to the detriment of the quality of the pulp.

The oxidizing action of HOCl is based on its readiness to break down into hydrochloric acid and oxygen. In the dark and out of contact with oxidizable matter this reaction is suppressed, but light and catalysts, such as iron and copper and their compounds, accelerate it. Some of the oxygen escapes from the solution as gas, and some of it reacts with HOCl to form $HClO_3$, which, under conditions permissible in bleaching pulp, reacts as an oxidizing agent so slowly that it is valueless as a bleaching agent. Any chlorine which is transformed to $HClO_3$ or to HCl with liberation of oxygen is lost to the process just as definitely as that which is volatilized to the atmosphere as HOCl.

Hypochlorites. The hypochlorites are salts of the very weak acid HOCl, and in aqueous solution they require the presence of free alkali to prevent the formation of HOCl by hydrolysis. Above pH 11 the HOCl is largely suppressed and the solution is relatively stable. Above a pH of about 8 the chlorine content of the hypochlorite reacts almost entirely by oxidation and has the same oxidizing capacity as it has in HOCl. The rate of reaction, however, is lower and decreases, while the stability of the solution increases, as the pH rises.

Bleaching powder is a dry, powdery combination of chlorine with hydrated lime. It contains about 15 per cent of free lime, which is essential to its stability during shipment and storage, and about 35 per cent of available chlorine, which value is accepted as the standard strength. The weight of bleaching powder used may be calculated to the equivalent weight of standard 35 per cent powder by multiplying by the percentage of available chlorine shown by analysis, and dividing by 35.

Clear solutions of hypochlorite may be prepared by agitating bleaching powder in water and allowing the excess lime and the insoluble impurities to settle, but this method has been almost completely displaced by that of injecting chlorine, usually in the liquid form, into lime milk. The lime milk is diluted to the desired concentration and the chlorine introduced until the pH drops to about 11.2, which is the point at which the addition of phenolphthalein causes a pink color which persists for 3 seconds. The progress of the chlorination can be followed by noting the rise in temperature of the solution; for each gram per liter of chlorine introduced there is a rise of $\frac{1}{4}$° C. Commercial solutions may be made at any concentration between 20 and 50 grams per liter of available chlorine, and in some cases have been made as strong as 90 grams. Under normal conditions at least 97 per cent of the chlorine added to the lime milk should be " available."

The reaction representing hypochlorite formation may be shown by the equation:

$$2Cl_2 + 2Ca(OH)_2 \rightleftharpoons CaCl_2 + Ca(OCl)_2 + H_2O$$

or stepwise:

$$2Cl_2 + 2H_2O \rightleftharpoons 2HCl + 2HOCl$$

$$2HCl + 2HOCl + 2Ca(OH)_2 \rightleftharpoons CaCl_2 + Ca(OCl)_2 + H_2O$$
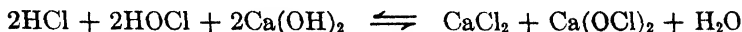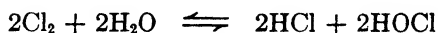
In acid media 4 chlorine atoms are " available " for chlorination; in alkaline media 2 oxygen atoms, equivalent to 4 chlorine atoms, are " available " for oxidation. All the chlorine added to the lime milk should, therefore, be " available," and if it is not, some reaction other than the formation of hypochlorite has occurred, as, e.g., the liberation of oxygen gas or the formation of chlorate or the reaction with impurities in the water or lime.

The concentration of bleach liquor is sometimes expressed in per cent content of bleaching powder, which always refers to powder of 35 per cent available chlorine strength. Consequently, available chlorine content divided by 0.35 gives the bleaching-powder content.

Soda bleach, a solution of sodium hypochlorite, is made by injecting chlorine — gas or liquid — into a solution of caustic soda. It is very similar to lime bleach in method of preparation, strength of solution, properties, and stability. It is used to some extent for bleaching rag stock, but for wood pulps its use is limited almost exclusively to the rayon or other dissolving grades.

The data of Table 47 are of interest in connection with the making of hypochlorites.

TABLE 47

	B.t.u. per Pound Chlorine	Calories per Gram Chlorine
Latent heat of vaporization of liquid chlorine................................	120	67
Heat of combination, Cl_2 + $Ca(OH)_2$....	648	360
Heat of combination, Cl_2 + NaOH......	630	350
Heat of hydration, CaO + H_2O........	486	270
Heat of solution, $Ca(OH)_2$..............	68	38
Heat of solution, NaOH................	447	248

1 lb. Chlorine combines with: 0.83 lb. commercial quicklime.
1.10 lb. commercial hydrated lime.
1.15 lb. caustic soda, 76%.
3.00 lb. soda ash.

1 liter bleach solution dissolves 1.8 grams $Ca(OH)_2$ (1.3 grams CaO).

Table 48 shows the change in composition of a bleach liquor over a period of nearly 6 months. This clear liquor was prepared[2] from bleaching powder, saturated with lime and its surface covered with oil to seal it from CO_2. It was stored in a container cooled by running water.

TABLE 48

Analysis No.	Date	Total Chlorine Grams per liter	Available Chlorine Grams per liter	Chlorates Grams per liter	Chlorides Grams per liter	Alkalinity Grams $Ca(OH)_2$ per liter
1	Aug. 15	49.6	36.6	3.85	9.6	1.18
2	Aug. 28	....	35.8	....	.....	....
3	Sept. 12	....	35.4	....	.....	....
4	Sept. 14	....	35.4	....	.....	....
5	Sept. 28	....	35.2	....	.....	....
6	Oct. 19	....	35.1	....	.....	....
7	Nov. 9	....	34.9	....	.....	....
8	Feb. 5	....	33.7	4.40	12.10	1.04

The total chlorides in this bleach are high in comparison with the available chlorine content, indicating that considerable decomposition of the bleaching powder had taken place before it was used to make up the bleach liquor.

Under normal operating conditions bleach liquor is sufficiently stable for all practical purposes if the following conditions are observed.

1. The liquor must contain an excess of lime sufficient to establish a pH of not less than 11.2.

2. Storage temperatures must not exceed 35° C. for a solution of 30 grams per liter available chlorine, or 40° C. for one of 20 grams per liter.

3. The solution must not come in contact with catalysts such as copper, nickel, and iron, or their salts. Iron and steel vessels and piping will be found satisfactory after they have become well coated with lime scale which protects the solution from direct contact with the iron rust.

4. Undue contact with the air must be avoided; CO_2 neutralizes the free alkali and lowers the pH to a zone of instability.

O'Neil and Rue[6] have shown that as the pH of the bleach solution is reduced below 11.2 it becomes progressively more unstable. The relation of the total and available chlorine content to pH is shown graphically in Fig. 40. When chlorinating this strength of lime milk, about 28 grams per liter of chlorine can be absorbed with little change

in pH, but thereafter its change is much greater in relation to the chlorine added.   Up to about 32 grams per liter, the available chlorine corresponds accurately to the total added; beyond this point, which is at a pH of about 9, the curves for total and available chlorine diverge, owing to the increasing combination of the chlorine into unavailable forms. After standing for 24 hours the divergence of the curves for total and available chlorine starts at a pH of about 11.2.

When a solution has become unstable by an excessive addition of chlorine or acid it can be restabilized by the prompt addition of enough alkali to bring the pH to at least 11.2.   If the pH continues to be low the available chlorine rapidly disappears with the formation of oxygen and chlorates.

Expressing Bleach Strength and Consumption.   When bleaching powder was the chief bleaching agent it was customary to express the amount used as the

FIG. 40.   PROGRESSIVE CHLORINATION OF Ca(OH)₂ SOLUTION.

equivalent amount of powder containing 35 per cent of available chlorine, and this practice was continued by some, even when the bleach liquor was prepared by absorbing chlorine in lime milk.   Others, however, expressed the concentration of their bleach liquors in terms of chlorine, with much resulting confusion.

It has been pointed out that all the chlorine added to water or to a solution of an alkali should be available for chlorination or for oxidation; in other words, it should be in the " active " form.   The " available "* or " active "* chlorine can be determined easily with arsenite

* These two terms are used commercially as synonyms.

or thiosulfate, and it is entirely proper to express the strength of reagents such as bleaching powder, or solutions of chlorine or hypochlorites, all in terms of active chlorine. When so expressed the total chlorine consumed in a series of reactions can be found by adding the quantities used in the individual reactions, even though some may be chlorinations and some hypochlorite oxidations. Since the introduction of the chlorination reaction into the bleaching procedure it has become the accepted practice to express the strength and the consumption of bleaching reagents in terms of active chlorine.

Another possible source of confusion is in the expression " per cent chlorine consumed," which is ambiguous in that it may mean either the proportion consumed as a per cent of the total added, or as a per cent of the weight of the pulp treated. Whenever the expression is used it should be made clear by some qualifying statement as to which meaning is intended.

BLEACHING SULFITE PULPS

Single-Stage Hypochlorite Bleaching. The hypochlorites react readily with sulfite pulps, many of which can be brought to a brightness of 78 to 80 in a single-stage reaction without serious loss in strength. For many years this was the chief means of bleaching such pulps, and the method is still used successfully in some mills. Even where other chemical reactions are used to remove part of the impurities, the hypochlorite stage effects the major portion of the brightening of the fibers, and the basic principles underlying its application are the same whether the reaction is carried on as a single stage or as one step in a multistage procedure.

As the hypochlorites may react with cellulose as well as with the impurities accompanying it, it is important to select such conditions of reaction that the chemical attack is chiefly on the impurities rather than on the cellulose. Excessive temperatures must be avoided; otherwise the rate of reaction becomes so great for both that practical selectivity is impossible and the cellulose fibers become seriously weakened before the impurities can be removed. High concentration of the hypochlorite has an effect similar to that of high temperature. The degree of alkalinity during the bleaching period also has a vital effect on the strength of the product; if the pH falls below 7.5 or 8, HOCl can be present in such proportions that the bleaching action may become too rapid and selective attack on impurities made difficult.

The consistency, or ratio of pulp to water, is important and is closely related to several other factors in bleaching. The approximate con-

sistency at which bleaching is done is usually established when the bleaching equipment is installed, since any major changes in consistency necessitate radical changes in the facilities for agitation, circulation, and blending. In general, consistencies of 3 to 4 per cent are found only in systems in which the pulp flows continuously from one tank to another while bleaching. For consistencies between 4 and 8 per cent, beaters, bellmers, and similar outfits are used, and recently special circulating equipment has become available for consistencies up to 9 and 10 per cent. For " high-density " bleaching at 12 to 20 per cent, still other types of equipment are required.

High-density bleaching must be done at temperatures not exceeding 28° C.; otherwise the attack on the impurities becomes less selective and the strength of the fiber suffers. This is an economic advantage, especially in cold climates and where steam cost is high. High density also favors cleanliness, as the high chemical concentration induces a more rapid penetration into the dirt specks which are hard to bleach. On the other hand it is difficult to blend the chemical with the pulp promptly and uniformly, despite the high power input for agitation, and the drastic kneading action involved may hydrate the pulp too much for some grades of paper. In such bleaches the quantity of water surrounding the fibers is so limited that diffusion of the soluble impurities from the walls of the fibers is kept at a minimum, and special care must be exercised in the washing operation to allow sufficient time for this to take place.

At low consistencies, i.e., 3 to 4 per cent, the chemical concentration in the liquid surrounding the fibers is low and a larger quantity is required than at high density in order to maintain the same concentration of residual chemical during the last part of the bleaching period. Because of the low chemical concentration the temperature must be correspondingly high — 40° to 50° C. — and the penetration of particles difficult to bleach is at a minimum, so the product tends to lack cleanliness.

The length of the bleaching period is determined by the temperature, the consistency of the pulp, and the brightness desired. For fully bleached chemical wood pulps the following are typical of commercial practice on the American continent:

CONSISTENCY OF PULP Per cent	TEMPERATURE °C.	PERIOD Hours
3– 4	40–50	5–6
5– 7	40–45	4–6
8–10	35–40	4–6
12–16	25–35	2–4

Chemical concentration also affects the length of the bleaching period, but economy and quality of product are both effective in limiting the quantity of chemical to only slightly in excess of that actually required. Chemical concentration may, therefore, be disregarded as a variable, except as it is a function of pulp consistency.

Consistency and the length of the bleaching period, taken together, determine the capacity of any given piece of bleaching equipment. The maximum period, as well as consistency, is, therefore, usually fairly well established when the equipment is installed; it should be set sufficiently high to allow for some variation in the hands of the operator. In continuous systems the installation establishes rather rigidly the bleaching period for any given rate of output, although some degree of variation can be effected through variation in the consistency.

Since the installation fixes the maximum pulp consistency and the maximum period for bleaching, the operator has available for control of his process the variables of temperature, length of period to a limited degree, and pH of the bleaching mass. Quantity of chemical is a variable but one governed by the requirements of the pulp and not subject to control at the will of the operator except at a sacrifice of economy of operation. Temperature and pH are probably the most important variables which can be so manipulated as to have a determining influence on the yield and the chemical and physical properties of the product.

To insure stability, the pH of the calcium hypochlorite solutions commonly used is always greater than 11, and the excess alkali present in the liquor usually establishes a pH of not less than 8 in the bleaching mass. During the early part of the bleaching period there is a rapid drop in pH, probably due to the formation of CO_2 and organic acids. Thereafter the pH declines at a slower rate and reaches an approximate condition of equilibrium at 6.4 to 6.8. Table 49 illustrates the change in pH as the active chlorine was progressively consumed when Mitscherlich sulfite was bleached with 19.5 per cent bleaching powder (6.8 per cent available chlorine) at 15 per cent consistency.[13]

Unless the initial pH of the bleaching mass is greater than 9, the pH at the end of the bleaching period is likely to fall below 6.4 and the brightness will also be low.[1] As the initial pH is increased from 9.3 to 11.9 the end pH remains fairly constant between 6.4 and 6.6 and very little change occurs in the bleaching time or the brightness of the product. A still further increase in the free alkali content, however, results in a progressive increase in the time for bleaching but also in an improvement in the brightness.

If the pH falls below 7.5 or 8.0 for a major portion of the bleaching period three undesirable conditions may prevail: (*a*) a portion of the available chlorine may react by chlorination; (*b*) a portion of the HOCl, which is present under these pH conditions, may be lost by volatilization or by decomposition, in which case the residual chlorine may not be sufficient to effect the desired brightening of the pulp; or (*c*) the HOCl may react so rapidly that the cellulose will be attacked and the fibers lose strength. For these reasons it has been found desirable in many commercial operations to raise the pH of the bleaching mass by the addition of lime or caustic soda.

TABLE 49

Time	pH	Bleach Remaining
Hours		Per cent
0	9.60	100.0
$\frac{1}{4}$	....	60.0
$\frac{1}{2}$	7.50	45.6
$\frac{3}{4}$	....	38.3
1	7.15	34.1
$1\frac{1}{2}$	6.85	....
2	6.70	20.5
$2\frac{1}{2}$	6.60	16.3
3	6.55	11.8
$3\frac{1}{2}$	6.47	8.8
4	....	6.5
7	6.47	1.9

In Fig. 41 is shown how adding lime to a hypochlorite bleach affects the pH and the rate of chlorine consumption.[9] The lime was added at the start of bleaching, and the tests were made on a sulfate pulp which had previously been purified by chlorination and caustic extraction.   In each case there is a period of rapid drop in pH, i.e., of rapid formation of soluble acid products.   As the total available lime in the solution is increased (curves *B* and *C*), the rapid drop in pH is delayed, which results in raising the pH at the end of the reaction and also in causing a larger portion of the reaction to take place under more alkaline conditions.

Excessive amounts of lime (curve *D*) greatly retard the rate of chlorine consumption and brightness development and in commercial operations may so lengthen the period of bleaching as to limit unduly the output with the available equipment.   A good practical rule is to add an amount that will maintain a pH not less than 7.5 or 8, even to the end of the bleaching period.   Under these conditions the stock will

react faintly pink to phenolphthalein when the bleaching is finished. The alkali is sometimes added in two or more portions successively applied as the bleaching proceeds; in this way excessive alkalinity does not retard bleaching so much in the early part of the process.
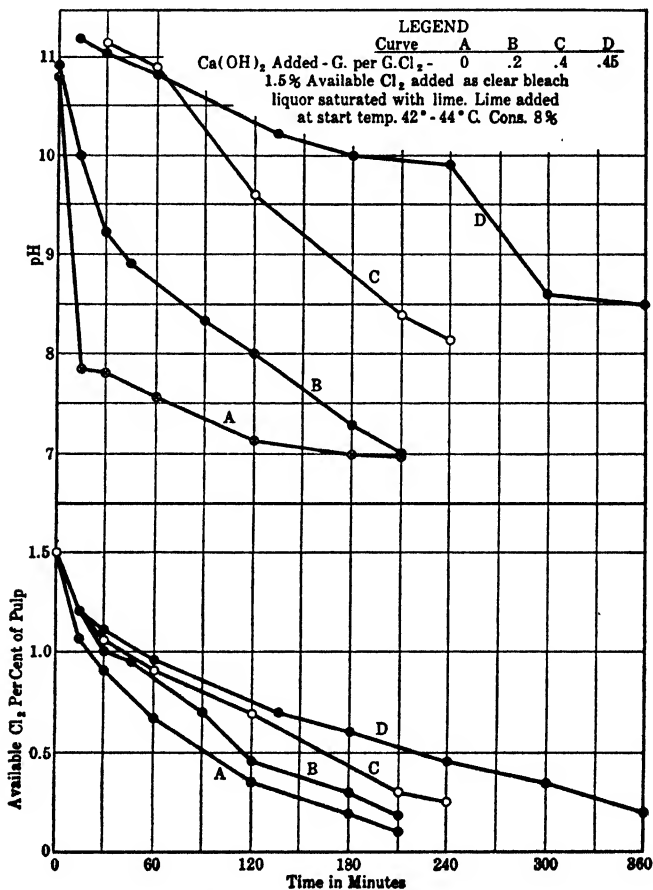
FIG. 41.   EFFECT OF LIME IN HYPOCHLORITE BLEACHING.

Some of the benefits of controlled alkalinity are improved brightness, greater uniformity in color, and improved strength in the pulp.

The addition of acid to a hypochlorite bleach speeds up the rate of consumption of the bleach and of increase in brightness of the pulp. Some mills in single-stage operation have long practiced this, especially during the latter part of the bleaching period where the action is slow owing to the low concentration of chlorine.   If the acid is added too

early, or in too large amounts, some of the chlorine may enter inefficiently into chlorination reactions or escape as free gas, and the HOCl may attack the cellulose, resulting in an excessive loss of yield and a serious reduction of the pulp strength.

An increase in temperature increases the rate of consumption of the available chlorine. Curran and Baird[2] give the following data when bleaching sulfite at a pulp consistency of 5 per cent, with bleach liquor containing 4.3 per cent available chlorine based on the oven dry pulp, and having a ratio of $Ca(OH)_2$ to chlorine of 0.033 to 1:

Temperature °C.	Period for 100 Per Cent Consumption of Cl_2	Loss in Weight
	Minutes	Per cent
21	713	2.0
35	220	2.0
41	128	3.4
46	83	4.9

The rate of reaction is approximately doubled for each 7.5° C. rise in temperature, and the rate of attack on the cellulose is, of course, also increased. A temperature must be selected which will effect the desired degree of purification and brightening with a minimum of attack on the cellulose.

Low temperatures retard the rate of diffusion of the chemicals into, and of the soluble reaction products out of, the fiber walls. They also lengthen the bleaching period, which will permit excessive attack on the cellulose and necessitate bleaching equipment of greater capacity. In general the temperature may safely be raised as the consistency of the pulp is decreased. Contrary to the table of typical American practice, some investigators recommend for the final hypochlorite reaction a temperature of 35° C. and a consistency of 5 to 6 per cent as most favorable for the production of brightness and for the removal of impurities.

Bleaching is an exothermic reaction, liberating 1100 calories for each gram of available chlorine consumed.[8] Pulp at 5 per cent consistency reacting with 5 per cent chlorine would cause a rise in temperature of about 3° C., and at 15 per cent consistency the rise would be about 9° C. To prevent the development of excessive temperatures during high-density bleaching it is important that the initial temperature be low; this is especially true for single-stage bleaching where the consumption of chlorine is relatively large.

Two-Stage Hypochlorite Bleaching. In bleaching pulp some of the oxidation products dissolve before the desired brightness is attained,

but continue to consume bleach. By bleaching the pulp in two hypo-chlorite stages and removing the soluble products by an intermediate wash before the second stage is begun, less bleach is required to produce the desired brightness and an improvement in the strength of the pulp usually results because of the lower strength of the bleach solution. The greatest saving in bleach is effected by using 40 to 60 per cent of the total bleach in the first stage.[5]

Dividing the operation into two stages does not shorten the total period of bleaching, but rather increases it by approximately the time required for the additional stage. In the second stage the quantity of bleach required has been reduced, but so has the initial concentration of chemical, and the net result is that the second stage in all its other operating conditions is substantially the same as the single stage.

The saving in chemicals, as compared with single-stage bleaching, is around 15 per cent, but this is offset to a greater or less degree by the increased cost involved in the installation and operation of two stages. The net economy is generally questionable, and a combination of two stages of hypochlorite is rarely found, except as it may be combined with other reactions of purification to form a bleaching procedure of three or more stages.

Two-Stage Chlorine-Hypochlorite Bleaching. Lignin is one of the most important impurities which react with hypochlorite and which, in single-stage bleaching, require the initial addition of relatively large amounts of chemical. Fortunately it has been found possible to remove lignin without appreciable attack on the cellulose by chlorinating the pulp at a pH of 2 or less. The chlorination proceeds with great rapidity, even at temperatures only slightly above 0° C. and at pulp consistencies of 3 or 4 per cent or even less, and the period of reaction need not exceed an hour. The products of chlorination are HCl (containing 50 to 80 per cent or more of the total chlorine added) and chlorinated organic compounds. Some of these compounds are sparingly soluble in water and some are insoluble, but in general they are more soluble in water containing caustic soda.

In practice the pulp is chlorinated in batches or in continuous flow at 3 to 4 per cent consistency, and washed on equipment which is rubber covered to resist the corrosive action of HCl and residual chlorine. Where such equipment is not available the chlorinated pulp may be neutralized with lime or caustic soda before washing. Caustic soda yields a more highly purified cellulose but is too costly, and lime-neutralized pulp bleaches to a product which in brightness and other properties is entirely suitable for all paper-making purposes except

those of a highly specialized character. Normally the length of the acid chlorination period is between 30 and 60 minutes, but several installations for continuous chlorination are in successful operation in which it is limited to approximately 5 minutes, after which the pulp is neutralized with lime and immediately washed. The temperature in this stage is rarely controlled and varies according to season and location between 1° and 25° C.

The greater the degree of chlorination, the less is the amount of hypochlorite required in the second stage, and the best quality of product is obtained when the available chlorine demand in this stage is not over 0.5 per cent, based on the pulp. It is entirely practicable from an operating standpoint to push the chlorination to this extent, but from the viewpoint of cleanliness of product it is frequently unwise. Many of the dirt particles finding their way into the unbleached pulp from the resinous portions of the wood, from knots, inner bark, etc., are penetrated with difficulty and are scarcely attacked during the relatively short part of the chlorination period in which there is an appreciable concentration of chlorine. In the subsequent hypochlorite stage the fibers are so easily bleached and the concentration of bleach so low that the dirt particles remain highly colored. In general, then, the cleaner the unbleached pulp the higher the degree to which it may be chlorinated with safety, and the greater the demand for cleanliness in the paper, the more carefully must these factors be controlled.

After removing the major portion of the bleach-consuming chemical by chlorination and washing, the brightening may be attained by means of a relatively small amount of bleach, a fact which is favorable to the maximum retention of the strength of the fibers. This is especially striking when it is observed that the bleaching is done with around 0.5 per cent of chlorine on the pulp weight, as compared with 4 to 5 per cent in a single stage.

The consumption of available chlorine and the brightening of the pulp both proceed rapidly during the early part of the bleaching period. Table 50 (first, fifth, and next to last columns) illustrates these facts for a chlorinated sulfite pulp.

Reflectance curves, made with the aid of a General Electric recording spectrophotometer over the visible spectrum at wavelengths between 400 and 700 mμ are shown in Fig. 42. The curves were made* on samples of pulp taken at various stages during the hypochlorite reaction period. From the curves, it may be seen that the improvement

* The reflectance curves were made and the data calculated by the Munising Paper Company on samples prepared by the Hooker Electrochemical Company.

in reflection is greatest at the short wavelengths and least at the long ones. The data in Table 50, columns 6, 7, and 8, were calculated from the curves in Fig. 42, according to the procedure described by Arthur C. Hardy.[3]

The conditions of the bleaching stage of a two-stage chlorine-hypochlorite procedure do not differ materially from those already
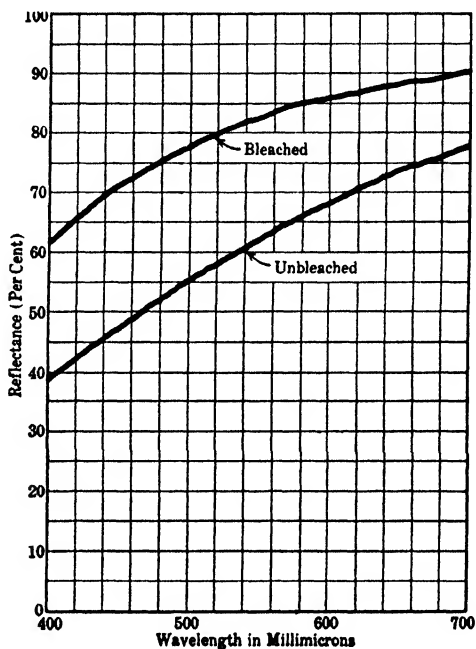
FIG. 42.   REFLECTANCE CURVES FOR SULFITE PULP.

described for the single hypochlorite stage, except for concentration of chemical. The alkali required to maintain the desired pH is somewhat less when the chlorinated pulp has been neutralized before washing than when it has been washed without neutralization.

The introduction of a chlorine stage prior to the bleaching stage results in a saving of 20 to 40 per cent of the chlorine and lime, and if the chlorinated stock is washed while acid, the lime saving is even greater. It produces a stronger pulp and permits the attainment of a higher degree of brightness, and it also makes it possible to bleach satisfactorily the less thoroughly cooked ("harder") pulps, provided that their properties are otherwise adaptable to the grades of paper to be made.

TABLE 50

DEVELOPMENT OF BRIGHTNESS IN A SULFITE PULP IN THE HYPOCHLORITE STAGE

The pulp had previously been chlorinated.

Period	Lime Added	pH	Temperature	Available Cl₂ Consumed (a)	Dominant Wavelength	Visual Efficiency	Purity	Brightness		
								W.P.M.A.	G.E. Reflection Meter	
								(b)	(c)	(d)
Minutes	Per Cent of Pulp		°C.	Per Cent of Pulp	mμ		Per Cent			
0	14	..	22	0.00	577.4	74.58	11.2	59.9	60.8	61.2
60	..	9.9	24	0.10	.....	.....	.....	.....	74.0	74.7
75	..	..	34	.....	.....	.....	.....	.....	.....	.....
120	..	8.3	34	0.45	575.8	85.55	7.1	72.4	74.7	75.0
125	7	..	..	.....	.....	.....	.....	.....	.....	.....
180	..	8.7	34	0.65	575.7	88.02	6.0	76.2	78.9	78.8
210	..	8.4	33	0.70	.....	.....	.....	.....	80.4	80.2
215	..	..	..	.....	.....	.....	.....	.....	.....	.....
250	1.5	8.5	32	0.90	575.8	88.32	4.0	78.8	81.5	80.6

(a) 1.8% available chlorine added.
(b) Readings made 2 weeks after those on the General Electric Reflection meter. W.P.M.A. (Writing Paper Mfgrs. Assn.) Brightness = Reflectance at wavelength 458.0 × 0.95.
(c) Readings made promptly after the samples were taken.
(d) Readings made 25 days after the samples were taken.

Bleaching Sulfite in More Than Two Stages. The two-stage chlorine-hypochlorite procedure has contributed, in large measure, to improvement in strength and brightness of product as well as to greater economy in chemicals consumed. In some mills still further improvements have been obtained by following the chlorination stage with two hypochlorite stages and washing after each.

Chlorine Required to Bleach Sulfite Pulps. The quantity of chlorine required to bleach sulfite pulps fully varies from about 2.5 per cent for easy-bleaching, to 7 or 8 per cent for hard-bleaching pulps. Within this range the actual consumption for a specific pulp varies according to whether a single-stage or a more complicated procedure is used.

It is frequently desirable to determine experimentally the amount of chlorine required to bleach a pulp, and several methods for determining the bleach required are discussed in Chapter XV. As explained there, the figures are chiefly comparative and will represent actual consumption of chlorine only when the tests are made to conform with the bleaching procedure to be employed. Once the test data are calibrated against operating conditions, they give valuable information to the bleach plant operator.

BLEACHING SULFATE PULPS

Sulfate pulps differ radically from sulfite pulps in their response to bleaching and purification reactions, and while sufficiently alike to be used interchangeably for many purposes, the bleached sulfates differ from the bleached sulfites in ways which permit them to meet some use requirements not satisfactorily met by the latter.

Unbleached sulfate pulps contain lignin and carbohydrate residues more or less polymerized by the action of the alkali in the cooking liquor, and these are slow to chlorinate and difficult to bleach. They also contain materials similar to the phlobotannins which may have been converted into sulfur dyes in the presence of sodium sulfide in the cooking liquor. These dyes may bleach to a light straw or cream color, but still be difficult to discharge completely.

Single-Stage Hypochlorite Bleaching. Hypochlorite, in single stage, readily bleaches sulfate pulps to a moderate manila shade (brightness up to about 55 to 60) without appreciable loss in strength, but it is not possible to bleach them to a full white by means of a single hypochlorite treatment. Attempts to force the brightness above the manila shades result in progressively greater loss in strength with only indifferent success in improving the brightness. This limits the single-stage procedure to the production of low, semi-bleached grades

whose brightness is lower than that of the unbleached sulfites. The chlorine consumed under these conditions will vary from 4 to 10 per cent, depending on the hardness of the pulp and the brightness attained.

It is important that the pH during bleaching does not fall below 7.5 to 8.0, otherwise some of the chlorine may react by chlorination to remove an unnecessary proportion of the lignin. If this happens it will decrease the yield and increase the chemical consumption and it may add nothing of value to the properties of the particular product in question.

Two-Stage Chlorine-Hypochlorite Bleaching. As the demand for brightness increases it becomes more and more important to use a two-stage chlorine-hypochlorite procedure. At the conclusion of each stage the pulp is washed, as only in this way can maximum economy of chemicals and strength of product be attained. For the lower shades it is unnecessary, from the standpoint of either economy or pulp quality, to purify the fibers by chlorinating the lignin, but, for the higher shades, chlorination is essential to adequate strength of product.

The two-stage chlorine-hypochlorite procedure is best adapted to the production of a bleached pulp having a brightness equal, or slightly superior, to that of unbleached sulfite pulps and a strength closely approaching that of the unbleached sulfate. For this purpose relatively hard-bleaching sulfate pulps may be used, with a total chlorine consumption ranging from 8 to 15 per cent, depending on wood species and the method of cooking.

The proportioning of the chlorine between stages has a far greater effect on strength of product than in the cases of sulfites. As the proportion used in the chlorination stage increases, that required in the subsequent hypochlorite stage decreases. At the same time, the strength of the final product increases until a maximum is reached. As the chlorine dosage in the chlorination stage is increased, the rate of reaction increases, but the period for exhaustion of the chlorine also increases.[10] (Note the slope of the curves and the reaction periods in Fig. 43.) The period of reaction may become so extended as to degrade the pulp strength and counteract the improvement resulting from the decrease of chemical in the hypochlorite stage.

It has been found desirable in several commercial operations to reduce still further the chlorine required in the hypochlorite stage. A large degree of chlorination reaction in a period of only 5 to 10 minutes has been induced by adding chlorine in excess of that which can be absorbed in the indicated period. By the addition of lime the pH is then raised from less than 2 in the chlorination stage to not less than 7.5, and as a result of the shift in pH the reaction of the chlorine is changed from

one of chlorination to one of oxidation. The chlorination stage thus becomes a sequence of two reactions: one under acid conditions for a period of 5 to 10 minutes, and the other under alkaline conditions for a period of 30 to 90 minutes. Operating under these conditions the degree of chlorination can be increased until the chlorine required in the subsequent hypochlorite stage is reduced to 0.5 to 1 per cent. The strength of the product is progressively increased and can be carried to values higher than those attainable without the alkaline phase of the chlorination stage.
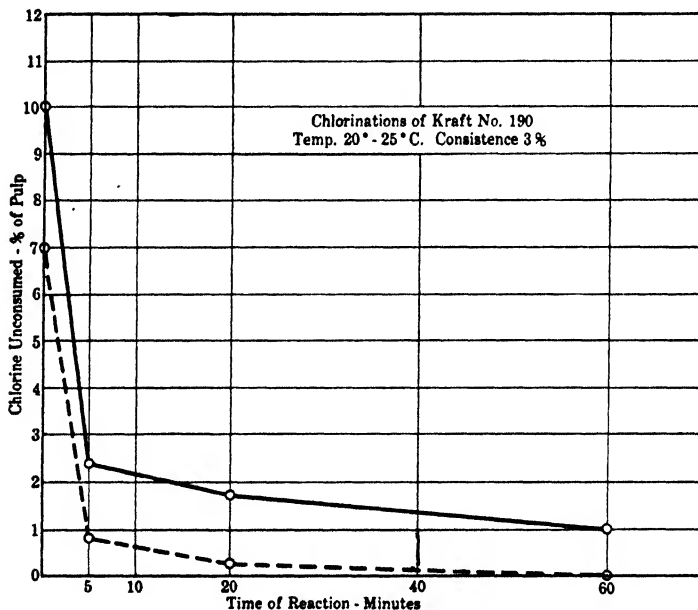
FIG. 43. EFFECT OF VARIABLE CHLORINE DOSAGE ON RATE OF CHLORINATION.

The consistency during chlorination is usually between 3 and 4 per cent, although values up to 5 per cent have been reported. It is desirable to use a maximum consistency compatible with ease in pumping and with facility in control of the rate of flow and with the degree of turbulence necessary to the solution and mixing of the chlorine with the pulp. A relatively high consistency is desirable also to speed up the rate of reaction during the slower oxidation phase of the two-reaction chlorination stage.

Temperatures up to about 27° C. may be maintained without serious harm to the fiber strength. At this temperature and a consistency of 3.5 per cent, the period of the oxidation phase of this stage should be

between 1 and 1.5 hours in continuous operation, and between $\frac{1}{2}$ and $\frac{3}{4}$ hour in batch operation.

As for the hypochlorite stage, the remarks under sulfite pulps apply. Too great emphasis cannot be laid on the importance, especially for sulfate pulps, of keeping the pH above 7.5 to 8.0 throughout the bleaching period.

Multistage Procedures for Full Bleaching. For the production of strong bleached pulps having a brightness in excess of about 70, a two-stage procedure is not adequate. There are still the dyes of the phlobotannin type which must be removed before the hypochlorite can produce the desired degree of brightening, and their removal by extraction with warm or hot caustic soda solutions has become the accepted practice. Partial removal can be effected by extraction of the unbleached pulp, but better results are obtained if the extraction is made on the chlorinated pulp, or that which has been given a chlorination and at least one hypochlorite treatment.

For full-bleached sulfate pulps the simplest procedure consists of three stages: (1) chlorination, (2) caustic extraction, and (3) hypochlorite oxidation, each concluded with a washing of the pulp. The discussion of the chlorination stage under the two-stage chlorine-hypochlorite procedure applies equally well here. The caustic stage follows logically after chlorination and serves to extract the dyes and to remove more completely the chlorinated products which may have escaped the previous washing. If the chlorination stage does not contain an alkaline oxidation phase it may be desirable to introduce a separate hypochlorite stage between an acid chlorination (followed by a wash without neutralization) and the caustic extraction stage.

In bleaching pulps for most paper-making uses it is not necessary that the caustic extraction be so drastic as to dissolve hemicelluloses and raise the alpha content of the pulp appreciably, and the proportion of caustic soda need not exceed about 2 per cent, based on the pulp. If the chlorinated pulp is washed without previous neutralization of acids a somewhat higher proportion of caustic is needed; in any event there must be an excess of free caustic to keep the dye in solution. The temperature may be between 50° and 100° C., and the higher it is the better the extraction, but also the higher is the cost for steam. The period of reaction is about an hour.

Thorough removal of the soluble impurities is of prime importance to prevent excessive reversion of brightness during drying and storage of the pulp or during wet storage. Neither caustic nor coloring matter is readily separated from the cellulose, so sufficient soaking time must

be given for diffusion of these impurities out of the cell walls into the surrounding water. For these reasons it has been found essential to wash twice with an intermediate soak of the pulp at 1 to 3 per cent consistency for a period of 1 to 3 hours.

The consumption of available chlorine in the hypochlorite stage should not exceed about 1 per cent on the weight of pulp, and should preferably be ½ per cent or less; the proportion of chlorine used in the chlorination stage must be adjusted accordingly.

The three-stage procedure: (1) chlorination, (2) caustic extraction, (3) hypochlorite oxidation, is suitable for bleaching sulfate pulps to a brightness of 70 to 75, or possibly higher, but for a brightness of 80 to 85 the hypochlorite treatment should be applied in two stages, making a four-stage procedure. A typical distribution of chemical consumption between stages would be as follows:

STAGE	PER CENT CHEMICAL ON PULP WEIGHT		
	Chlorine	CaO	NaOH
First: chlorination	9	8	...
Second: caustic extraction	...	..	2
Third: hypochlorite	0.5	..	0.3
Fourth: hypochlorite	0.3	..	0.2

The caustic in the third and fourth stages is for pH control.

Here again it is important to give two washes with an intermediate soaking. Removal of the last traces of alkali remaining from the hypochlorite stages is facilitated by adjusting the pH to 6 to 6.5 during the soaking period; this adjustment may be made with an iron-free acid, such as HCl or H_2SO_4, with chlorine water or with SO_2. The last possesses at least two advantages over the other two; it destroys any active chlorine remaining from the hypochlorite stage, and it reduces a portion of the iron and renders it more readily removable from the pulp. Ferric iron, if present in too large proportion, discolors the pulp and may also catalyze the chemical reactions which darken and weaken the fiber during storage.

For the production of very strong pulps having a brightness of 80 and above, the bleaching procedure should contain at least six stages: (1) chlorination, (2) caustic extraction, (3) soak, (4) hypochlorite, (5) hypochlorite, (6) pH adjustment and soak, each stage concluded with a wash. Economy of chemical consumption and probably quality of product may dictate that the chlorination should be performed in two stages. It is possible, also, that a caustic extraction should follow each of the chlorination stages. Installations containing all these stages are in operation.

BLEACHING SODA PULPS

Soda pulps from deciduous woods are short fibered and have been used chiefly as fillers rather than for any strength they might contribute to the paper. Until the last few years these pulps have been bleached single stage with hypochlorite, and in an effort to increase the brightness, which at best was around 70 to 75, overbleaching was not uncommon. It is now frequent practice to chlorinate the pulp prior to bleaching so as to improve the brightness still further. In the chlorination stage 30 to 50 per cent of the total chlorine is added and the chlorinated pulp is washed, either in the acid condition or after neutralizing with caustic soda. Not only is the brightness improved, but the strength is increased to such a degree that the pulps become a factor in the strength of the paper.

The change in brightness as the bleaching reaction proceeds is illustrated by the typical data in Table 51. The pulp had been chlorinated previous to bleaching.

TABLE 51

Period	pH*	Cl_2 Consumed	Brightness (G.E. Reflection Meter)
Minutes		Per cent of pulp	
0	. . .	0	45
30	7.6	0.7	67
60	7.7	0.8	69
70	8.0	. . .	. .
90	7.9	. . .	. .
120	7.7	0.9	70
150	8.8	. . .	. .
180	7.9	0.98	71

*Controlled by addition of lime at intervals during bleaching.

Some pulps of coniferous origin are prepared by the soda process either with or without the addition of some sulfur to the cooking liquor. Such pulps are best bleached in at least three stages: (1) chlorination, (2) caustic extraction, (3) hypochlorite bleach, each concluded with a wash. The introduction of the caustic stage contributes to high strength as well as to high brightness of the bleached product.

BLEACHING RAYON-GRADE PULPS

Chemical wood pulp, especially prepared, purified, and bleached, has assumed a prominent role as a raw material in the manufacture of rayon. Thus far such pulps in North America have been limited almost exclusively to those prepared by the sulfite process, chiefly from spruce

and western hemlock and to a limited extent from some of the hardwoods.

The pulps are cooked under conditions which insure a greater degree of purity of cellulose than is customary for paper-making grades, and the purification and bleaching procedures are somewhat analogous to the more complicated multistage procedures described for the bleaching of sulfate pulps. The caustic extraction is usually more drastic than for sulfate, and acid treatments are sometimes inserted to reduce the ash content. Viscosity, which is very important, is controlled within limits by adjustment of the pH in the acid extraction and bleaching stages. The final bleaching is done with sodium hypochlorite, because calcium hypochlorite results in a larger ash content in the pulp.

Other notes on the preparation and testing of such pulps will be found in Chapters VIII and XV.

ANTICHLORS

It is very essential that the washed, bleached stock should contain no available chlorine. Should there be a large excess in the bleacher when the desired brightness is reached, difficulty may be encountered in completely washing out the unconsumed residues. Such difficulties have led to the use of various chemicals to reduce and render the chlorine harmless; from the nature of the work they perform these are called antichlors.

One commonly employed antichlor is sodium thiosulfate (" hyposulfite of soda," $Na_2S_2O_3 \cdot 5H_2O$), which is added in dilute solution to the bleacher when the desired brightness has been reached. The products formed by the reaction with bleach may include HCl, $Na_2S_4O_6$, etc. If not washed out they are likely to exert a destructive influence on machine wires, and their presence in paper may be fully as harmful as the chlorine which they are intended to eliminate.

Safer antichlors are sodium sulfite and calcium sulfite, which form products less harmful than those from thiosulfate. Because of its slight solubility, calcium sulfite possesses the advantage that any excess acts as a filler and usually is harmless.

Other antichlors which have been proposed are the sulfite liquor used in making wood pulp; the mixture of calcium thiosulfate and polysulfide prepared by boiling sulfur with milk of lime; and hydrogen peroxide. The first of these is rapid and efficient in action but must be used with caution as an excess tends to set up acid conditions in the pulp, with consequent injury to wires, driers, and even the paper itself. The lime-sulfur mixture is probably even more injurious, since considerable amounts of free sulfur are precipitated on the fibers during the reaction, and this, because of its finely divided condition, is gradually oxidized

to sulfuric acid, which renders the paper brittle by formation of hydro-cellulose. The free sulfur also causes tendering of the machine wires through formation of metallic sulfides. Hydrogen peroxide is the safest of all the antichlors since it forms only water and free oxygen, but it is too expensive for commercial use.

There may be times when an antichlor is of assistance, but the regular use of such an agent indicates inefficient bleaching methods since expense is being incurred to destroy a portion of the bleach which should be employed in useful work. In a well-regulated mill it should be possible to operate without antichlors.

WASHING

The impurities rendered soluble by the various reactions of the modern bleaching procedures must be thoroughly removed at each stage of the procedure by washing the fibers with water. It is not unusual to find mills using 80,000 to 100,000 gallons per ton of pulp when bleaching in four or more stages. Counter-current use of water can be practiced to a limited extent, but care must be exercised that the re-used water does not contain impurities which will cause excessive chemical consumption or will precipitate on the fibers impurities already brought into solution. Wash water from a hypochlorite stage can be used to dilute, for the washer, pulp from an earlier hypochlorite stage, provided that fresh water is used for the final displacement of the impurities. The same wash water should not, however, be used to dilute pulp going to a hypochlorite stage, for under such conditions the impurities in the wash water would react with the hypochlorite and decrease the efficiency of the operation. Wash water containing the residues from a calcium hypochlorite bleach should not be used to dilute the unwashed pulp from the caustic extraction stage as the presence of calcium salts may precipitate some of the dyes which are made soluble by the caustic.

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CHAPTER X

SIZING

R. M. K. Cobb

In most of the uses to which paper is put the fibers must be partially or wholly non-absorbent to liquids, and for other uses the degree of absorbency has to be carefully controlled by what is known as the sizing process. Papers range in water absorbency from blotting paper, through water-resistant writing papers, to non-absorbent drinking-cup stock. In oil and grease absorbency there are at one end of the scale the highly absorbent electrical insulating papers and at the other end non-absorbent glassines.

Accurately stated, the sizing of paper is a treatment primarily designed to *reduce* the *rate of penetration* of liquids. In paper-making terms the *slower* the rate of penetration, the *harder* the degree of sizing. Sizing treatments are applied (*a*) internally by precipitation on the fibers in the beater, or (*b*) by surface treatment of the web of paper.

The mechanism by which sizing brings about resistance to penetration by liquids is most simply explained by the contact-angle theory proposed by Cobb and Lowe[14] in 1934. This theory of sizing follows from consideration of the equation of rate of flow into fine capillaries:

$$l^2 = \frac{r\sigma \cos \Theta t}{2\mu}$$

where l = depth of liquid penetration in centimeters.

r = paper pore radius in centimeters.

σ = surface tension of liquid in dynes per centimeter.

$\cos \Theta$ = cosine of angle Θ taken by liquid in contact with solid.

t = time of penetration in seconds.

μ = coefficient of viscosity in poises. μ water = 0.01006 poise at 20° C.

This equation has been developed or studied in exact or empirical form by Washburn[81] and others.[54,44,23,61,3,69,57]

According to the contact-angle theory of sizing, the function of internal or beater sizing is to reduce penetration of liquids into paper capillaries by raising the contact angle of the paper against those liquids,

while surface sizing reduces penetration of liquids by closing the pores of the paper, or by raising the contact angle of the paper against the liquid, or by doing both. The sizing of paper involves the properties of the liquid which is penetrating it as much as it does those of the paper itself, and to all intents and purposes a change in the surface tension, viscosity, or contact angle of the penetrating liquid affects the " sizing " of paper as much as does a change in the pore radius or contact angle of the paper itself.

The contact-angle theory expresses in exact form the opinion voiced in 1923 by Thiriet and Delcroix[75] that sizing was not effected by changing the porosity of the paper but by changing its surface tension.

It is important to note that the contact angle of water toward rosin-sized paper is high, while that of the oily base of printing ink is low. There is, therefore, no relationship between the resistance of paper to water and to printing ink, and to make a " printability " sizing test with water is as foolish as it is wrong. Printing paper may absorb water instantly, yet allow so little printing ink to penetrate its surface that it will offset badly, or it may be sized internally with rosin to such an extent that it will hold water for days, yet absorb printing ink into its open pores so readily that no offset of ink will take place.

Secondary Effects of Sizing. The sizing materials used to reduce the penetration of liquids also cause important secondary effects. Hammill, Gottschalk, and Bicking,[24] Strasser,[72] and others show that surface sizing with glue or starch may increase bursting strengths as much as 40 per cent, and it is commonly believed that even rosin size has some favorable effect on the hardness of a sheet. Weber and Cobb[82] found that ordinary surface sizing tended to increase misregister slightly on lithographic presses and that the same result was caused by rosin sizing. They also found rosin-sized sheets less soft and fuzzy than unsized paper made from the same beater of stock, but that a bare minimum of sizing was necessary to effect this desirable result.

Unlike ordinary printing papers, litho papers need a certain degree of water resistance to withstand the fountain water transmitted to the sheet on each impression. The effect of internal sizing and surface sizing on the strength and misregister of lithographic papers is shown in Table 52. In this work the distances between register marks were 35.3 and 50.15 inches.

Sizing is generally supposed to decrease the rate of change of moisture when paper is brought into the pressroom, but no accurate study of the problem has ever been made. Neither is it known whether sized or unsized paper is the more likely to curl and warp when exposed to an atmosphere with which it is out of equilibrium.

TABLE 52

Effect of Internal Sizing

Amount of size used	0	½ Normal	Normal
Indicator sizing test..................	19.1 sec.	23.1 sec.	26.3 sec.
Cobb test, 2 min.....................	46.0 g/M²	26.8 g/M²	11.0 g/M²
Mullen per 0.010 in. test..............	68	63.5	57.5
Double folds across grain.............	55	48	38
Misregister in long direction..........	−0.045 in.	−0.014 in.	−0 014 in.
Misregister in short direction.........	−0.018 in.	−0.024 in.	−0.032 in.

Effect of Surface Sizing

	Gently Beaten Stock		Hard Beaten Stock	
	Untreated	Surface Treated	Untreated	Surface Treated
Pop per 0.010 in........	49.5	53	52	68.5
Double folds *vs.* grain.....	52	12	14	55
Misregister in long direction..............	−0.006 in.	−0.014 in.	0.014 in.	−0.016 in.
Misregister in short direction..............	0 in.	+.003 in.	−0.003 in.	−0.003 in.

Surface Sizing. The term " tub sizing " formerly referred to a treatment given to dried papers, but in order to embrace many of the newer processes it is advisable to broaden the term to " surface sizing " and include any sizing treatment applied to the web after the moment of formation on the wet end of the machine.

Paper is surface-sized to close the pores and prevent the feathering of aqueous writing ink, either on the first lettering or after erasing; or to increase the surface strength and resistance to picking of fibers in printing; or to make the surface smoother and reduce the absorption of printing ink.   Pigments are now being included in surface sizing in attempts to impart, upon the paper machine itself, some of the desirable properties of coated papers.

Surface sizing influences writing and printing qualities, and to some extent coating and laminating, and the properties imparted may differ from those given by internal sizing.   A sizing film too thin to be perceptible by internal sizing tests, yet effective against the small amount of aqueous ink carried on a pen, may be applied at the size tub or on the calender.   Conversely the surface of the paper may be desized for the depth of a micron or two, as a result of the solvent action of hot water

at the water boxes, and this will show up on the surface as feathering with ink, though too slight to show in the regular internal sizing tests.[16]

Surface sizing also differs from internal sizing[14] because a drop of liquid tends to penetrate down *into* empty capillaries more readily than it tends to spread sideways over the surface of the sheet.

Glue. Of the materials which have been proposed for use in surface sizing, none is used in appreciable quantities except glue and starch, and of these starch is the more largely employed. For high-grade papers the best glue, known as gelatine, should be used. Pure gelatine is a colorless, odorless, nearly transparent, nitrogenous substance which is insoluble in cold water but swells and absorbs three or four times its weight when soaked in it. In hot water it dissolves readily, and a strong solution sets to a firm jelly on cooling; even as little as 1 per cent gives a gelatinous mass. The purest commercial form of gelatine is isinglass, which is made from the swimming bladders of various kinds of fish; below this in quality are the different grades of hide glue, and still lower are the bone glues. Many glues are excluded from sizing work because of their poor color and others because of their low gelatinizing power.

Some paper makers still make their own glue, but usually it is better to purchase a gelatine or glue of standard quality. It is more likely to be uniform, and it has been claimed that size made from air-dried glue is superior to that made from the original jelly. This seems to be contradicted by Klein and Minor,[34] who compare mill-made and purchased dry glues for fine papers and find the viscosity of mill-made glue better than that of purchased glue. The gelatine which gives the firmest jelly is considered the best sizing agent, and the higher-priced gelatines will usually be found the cheapest in the end because of their greater efficiency. Saxl,[61] however, points out that this is not always true.

Glue solutions used in sizing generally vary between 4 and 7 per cent solids, and the temperature of application may range from $85°$ to $120°$ F. Alum is frequently added as a preservative and to aid in preventing spoiling of the sized paper in damp air. On adding alum the glue solution thickens, and as the amount is increased it may almost form a jelly; if still more alum is added the solution becomes thin again and may be even more fluid than the original solution. This offers a means for controlling the penetration of the size into the paper, since this depends in part on the fluidity of the solution. The percentages of gelatine, based on the original dry paper, absorbed from a 5 per cent

solution, with and without alum, by papers sized with different amounts of rosin are as follows:[17]

Percentage of rosin size	0.0	0.5	1.0	1.5	2.0	2.5
Gelatine absorbed, no alum used	12.1	10.9	8.9	8.0	7.2	6.5
Gelatine absorbed, 8 per cent alum used	10.2	9.1	7.5	6.5	5.7	5.2

Another substance occasionally added to the size solution is soap, which is claimed to have a certain lubricating effect on the fibers, to improve the opacity, and to disguise the color of poor glue. The soap is dissolved to a clear solution in water and added to the glue solution before the alum, the addition of which decomposes the soap. Not every kind of soap is suitable for this work as it must be such that the addition of alum produces a fine emulsion rather than a curdled mass of fatty acids.

The mechanical operations in surface-sizing sheets of paper were originally of a comparatively simple nature; the sheets were suspended in the hot size until the air was expelled, the excess of size removed by pressing, and the sheets hung up to dry. The sheets were sometimes fed into the size solution in a vat between endless felts which had to be long enough to give time for the air to escape from the paper. This process was expensive for unsized papers because of the cost of handling single sheets and the large amount of size absorbed. This latter depended on the viscosity, temperature, and strength of the glue solution and the condition of the paper. Free stuff absorbed more glue than wet beaten stock, while bone-dry paper absorbed it less rapidly than that with an appreciable amount of moisture.

In America practically all surface-sized paper is made as a part of the paper-machine operation by leading the web through a trough filled with the size, kept at the desired temperature by continual circulation to and from the supply tank. This method enables the paper to be beater-sized with rosin and partially dried by passing over a few cylinders before reaching the size trough, so that the amount of glue absorbed is materially reduced. If the paper is reeled'up, after the excess of size is removed by squeeze rolls, and allowed to season a short time before drying the sizing is improved, but in many cases it passes directly from the squeeze rolls to the dryers, which are skeleton drums around which the paper passes and within which are fans to keep up a circulation of air.

The drying of glue-sized papers is particularly important because the quality of the product depends largely on this operation. Slow drying without agitation, and at a temperature below the liquefying point of the jelly, is desirable, so the problem is really that of drying a jelly rather than a solution. Loft drying is the best but the slowest and

most expensive; the festoon arrangement used in drying coated papers gives fair results, while if the paper is dried on steam cylinders the glue has little sizing power, since a continuous film is not formed. Paper dried on skeleton drums is subjected to so much vibration from the fans that the surface tends to crack and the product is inferior to loft-dried paper. Sizing which is found to be defective after drying may sometimes be improved by wetting and again drying. The temperature of drying depends in part on the atmospheric humidity. If this is low, drying takes place rapidly and a correspondingly low temperature may be employed, but if the humidity is high the temperature must be raised to permit evaporation to take place. The upper limit is set by the liquefaction of the sizing, which usually takes place at lower temperatures with poorer grades of glue than it does with gelatines.

Surface sizing with glue is apparently a simple operation, but in reality it is one of the most difficult and uncertain of all those carried out by the paper maker, since the gelatine is so greatly affected by atmospheric conditions and its absorption is so dependent on the physical and chemical conditions of the paper employed.

Surface sizing makes paper stronger and firmer and gives a better surface for writing than does engine sizing. Its effect is reduced by subsequent calendering, rolling, or plate glazing, which explains why papers with a rough surface are more easily hard-sized than those which are highly glazed.

Studies of the effect of surface sizing with glue upon the physical properties of the paper[24] have shown that increased retention of glue increases the bursting strength, while the folding endurance increases up to a certain point and then decreases. The resistance of glue-sized papers to water and wet rubbing may be considerably increased by treating the sized but undried papers with glue hardening agents, such as formaldehyde, but the process must be carefully controlled, or the folding endurance will be injured. The addition of softening agents or lubricants, such as glycerine or non-drying oils, increases the folding endurance of the paper, whether it is unsized, rosin-sized, or surface-sized, but the effect of glycerine appears to be comparatively short lived.

Glue or gelatine for surface sizing should be tested for grease, acidity, ash, added alum, and firmness of jelly. Methods for the first two are mentioned briefly in Chapter XIII. Ash may be determined by burning a weighed sample in a porcelain crucible and weighing the residue. The presence of alumina in the residue indicates that alum may have been added to give greater thickness to the glue solution, and that the jelly test will, therefore, not show the true sizing value of the glue.

The jelly strength may be determined numerically by preparing jellies of a given strength of solution and noting the time required for a definite weight to penetrate for a given distance, or by determining the force required to remove a plunger around which the jelly has been formed. Jellies prepared in the same way from the sample and from a standard glue may be compared.

Starch. Starch is largely used in surface sizing in place of glue. Solutions of the natural starches are too thick to be applied at the usual concentrations, and if they are reduced to the proper fluidity, so much water is needed that enough starch to be effective is not present. The so-called modified starches which are used for this work are dissolved by heating in water and applied either with or without the addition of soap, wax, or other chemicals, in much the same way as glue size. They give firmness and rattle to the paper but do not size so well against writing ink as do animal sizes, nor do they impart so much strength. This is due to their lower structural strength, and the fact that a firm gel is not formed on cooling and hence the spaces between the fibers are not filled.

A review of the differences between the structural strength of glue, gelatine, and starch is given in a report of the British Adhesives Committee.[9]

An important recent development in surface sizing is the use of enzymes to modify the starch, the earliest reference to this having been published in 1893.[42] The process has been described more recently by Diehm.[21] The conversion is carried out by mixing the starch with cold water, adding the enzyme, and heating to about 160° F., holding at that temperature until the enzyme has converted the starch, and then destroying the enzyme by heating to 185° F. or higher. For the best results the pH must be held between about 6.4 and 7.2, and no antiseptic must be present or it will prevent the action of the enzyme. Conversion takes place in 15 to 30 minutes. The advantage of enzyme conversion is that, with one grade of raw starch, the paper mill is able to obtain solutions of almost any desired fluidity and concentration. Cost is also lower than for chemically treated starches.

Starch Beater Sizing. The use of starch in the beater may be discussed at this point as a link between starch sizing on the dry end of the machine and beater sizing for water resistance, in which rosin size is employed. Starch is used in the beater to strengthen and stiffen the paper and to decrease fuzz. Of the kinds available, the choice is generally that which can be obtained most cheaply, due regard being paid to quality. In normal times cornstarch is used largely in this country, while in Europe potato starch is generally employed. In recent years

cold-water dispersible potato and tapioca starches have found considerable use. These are made by passing starch and water over a heated cylinder which cooks, swells, and dries the product in one operation. When added to the beater they swell and partially disperse.

Unmodified starch is added to the engine either in the raw condition or after boiling with water. The retention of the raw starch is undoubtedly greater than that of the boiled, but its effect in hardening the paper may not be any greater, since, in order to accomplish this, it must be gelatinized in passing over the driers. Examination of papers made from stock containing raw starches shows that many granules are not even swollen, and such can have little value except as a filler.

Strasser[72] presents the results of a survey on the use of starch for beater and surface sizing in paper mills throughout the United States. The starches most generally used were untreated tapioca and corn. About 80 per cent of the mills used cooked starch, and when a modified starch was used it was generally an oxidized form. The survey was made before the introduction of the enzyme treatment.

From investigations at the Institute of Paper Chemistry, Strasser concludes that starch is held in paper mechanically and is not adsorbed. He believes that less than 1.5 per cent develops insufficient strength, while above 4 per cent it costs too much for the additional strength obtained.

Because of the difficulty of accurately determining starch in the presence of cellulose there is little reliable information regarding the percentage retained. Lutz[45] has shown that retention varies with the kind of starch and the condition when added; with hand-made sheets from stock to which 10 per cent of starch had been added he obtained the following retentions:

KIND OF STARCH	RETENTION WHEN ADDED	
	RAW	BOILED
Potato	73.6%	46.2%
Wheat	71.7%	58.3%
Rice	53.4%	58.9%

With raw starch the larger grains are retained better, while if the starch is boiled, better retention occurs with those starches which give the stiffest pastes. Probably such high retentions as these are not realized in machine-made papers where the chances for loss are so much greater.

Working under conditions of definite starch retention, Cobb, Lowe, Pohl, and Weiss[15] found that the desirable effects of hardening, increasing strength, and surface reinforcement went through a maximum

at a starch content which varied with the degree of enzyme modification of the starch as shown in Fig. 44.

In confirmation of the maximum region, they also found that, when the previously published data of Weber, Shaw, and O'Leary[83] were recalculated to the basis of 0.010 in. gage, the maximum Mullen test was obtained at 0.5 per cent starch retained in the sheet. They conclude that starch acts to increase the water content of the wet-pressed sheet, increases the Mullen by increasing the solid fraction of the dried paper,
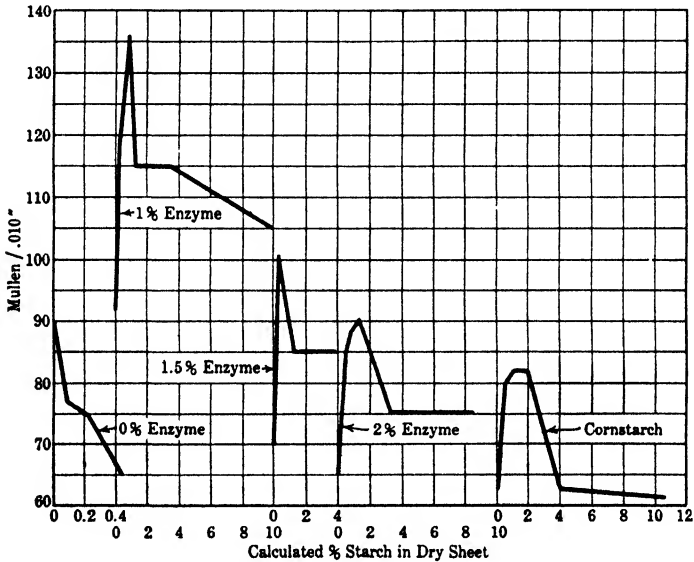
FIG. 44.   MULLEN vs. PER CENT STARCH IN SHEET.

and increases resistance to fuzzing and picking by binding fiber to fiber independently of the solid fraction. They believe that the fact that strength properties go through a maximum indicates that the starch structure per se is weaker than the cellulose structure.

In contrast with these ideas another worker has found that, if unconverted boiled tapioca starch is used with alum and soda in such a manner that practically all the starch is retained in the hand-made sheets, the bursting strength increases continuously from no starch up to 6 per cent.

While this work outlines what happens when starch is present in paper, how to get 0.5 to 1.0 per cent of starch in effective form into a sheet is another problem. Several processes are claimed to accomplish this. In one the starch granules are swollen by heat in the presence

of silicate of soda. In two similar processes, patented by Pattilloch[55] and described by Rowland,[60] the starch is precipitated in the presence of soda or sodium aluminate. The theory is that, although both starch and fiber are negatively charged, when alumina is thrown down on the fiber the starch is carried along with it. The process is not effective with converted starches. The film precipitated on the fibers is very delicate and is easily destroyed by vigorous agitation, which somewhat limits the practical application of the process.

Lee[41] describes the microscopic examination of starch-treated papers; he finds that uncooked starch shows as granules throughout the web, while cooked starch added to the beater seems to migrate to the surface of the sheet leaving only empty husks in the center. Surface sizings, microscopically examined, seldom appear to form a continuous, non-porous film.

Engine Sizing. Surface sizing is too slow and expensive when only water resistance is desired, and for most modern papers sizing is effected internally by raising the contact angle of the fibers against water, leaving the pores open. Illig[27] discovered the principle of rosin sizing more than 100 years ago, and present processes follow closely that original discovery, depending upon the precipitation on the fibers of some material such as rosin or wax, which upon drying forms a water-repellent film. As this operation generally takes place in the beating engine it is called beater or engine sizing.

TABLE 53

MATERIALS USED IN SIZING

Rosin: A nearly tasteless, brittle resin; mol. wt. 302.24; sp. gr. 1.07–1.08. Softens at 158°–176° F. Insoluble in water. Soluble in methyl and amyl alcohol, acetone, ether, carbon disulfide, chloroform, fixed and volatile oils. Dissolves in alkalies to form soaps. Acid number 155–175. Unsaponifiable matter 4–10 per cent. Contains 0.1–6.7 per cent insoluble in petroleum spirit, the amount increased by sunlight; the insoluble matter is devoid of sizing power. Rosin consists of 85 per cent rosin acids, 5 per cent esters, and 10 per cent resenes. One constituent, abietic acid, forms a sodium salt, consisting of 3 molecules of abietic acid and 1 of sodium abietate. Gum rosin is obtained from the distillation of turpentine. Grades: A, black, to WW, water white; F and G most commonly used in sizing. Wood rosin is obtained by extraction of wood and stumps; formerly had a very poor color, but has recently been much improved. Analysis, T.A.P.P.I. method T621m.

Paraffin waxes: Scale and other crystalline waxes are white solids obtained from residues of oil stills. Sp. gr. 0.88–0.915. M.p. 120–130° F. They consist of inert, unsaponifiable hydrocarbons; readily emulsified.

Amorphous paraffin waxes vary from vaselinelike materials to hard waxes. M.p. 150°–160° F. Yellow to dark brown in color. Soluble in benzene, warm alcohol, turpentine, chloroform, carbon disulfide, and olive oil.

TABLE 53 — *Concluded*

Montan wax: A very hard mixture of organic acids, hydrocarbons, and esters. M.p. 180° F. Very water resistant. Acts as stabilizer of emulsions when added to paraffin wax.

Alum: Paper-maker's alum consists of $Al_2(SO_4)_3$ with somewhat varying amounts of water, usually about 43 per cent. The Al_2O_3 content is approximately 17 per cent. Sp. gr. 1.62. Soluble in water. pH of a saturated solution 2.3, and of a solution at 2.0 grams per liter 4.0. Made by dissolving bauxite in sulfuric acid. Should be nearly iron-free, upper limit being about 0.07 per cent. Basic alum contains 0.10–1.0 per cent excess Al_2O_3. Acid alum contains up to 0.5 per cent free acid. Analysis, T.A.P.P.I. method T614m37.

Sodium aluminate: $Na_2Al_2O_4$. Mol. wt. 164.2. White hygroscopic flakes, soluble in water. Contains aluminum in the negative instead of the positive radical. Is used for supplementing alum to precipitate size in the higher pH range.

Soda ash: Anhydrous light sodium carbonate, Na_2CO_3. Mol. wt. 106. Sp. gr. 2.476. Contains 58 per cent Na_2O. One hundred pounds rosin require about 16 lb. of soda ash. Analysis, T.A.P.P.I. method T612m.

Preparation of Rosin Size. Most methods of making rosin size are based on the principle of combining the acid rosin with an alkali to render it soluble. The alkali commonly used is soda ash, which is said to give better results than caustic soda. The relative value of these alkalies probably depends on local conditions, and sometimes the size made with caustic soda is more efficient than that prepared with soda ash.

One very general mode of operation is to boil in an open kettle fitted with a steam coil or jacketed around the bottom. The rosin may be added first and melted, and then the soda ash, dissolved in the desired amount of water, run in, little by little, or the soda ash may be dissolved in the kettle and then crushed rosin added to the boiling solution. The time of boiling varies from 3 to 7 hours, but even with very long boiling it is not possible to cause all the soda ash to combine with the rosin, so the final product generally contains both free rosin and uncombined soda. In one mill using 400 pounds of soda ash for 2000 pounds of rosin and boiling for 3 hours the size made analyzed as follows:

	FRESHLY PREPARED	READY TO USE
Combined rosin	22.0	30.5
Free rosin	11.3	15.9
Combined soda, Na_2O	3.0	4.5
Free soda, Na_2CO_3	3.4	1.2
Water by difference	60.3	47.9

Krimmel[37] reports in a study of size making a loss of 5.27 per cent in the conversion of the rosin to soap; 6.84 per cent in converting the

soap to milk; and 15.36–17.7 per cent loss due to barrels, the rosin being purchased by gross weight. He also finds, in analyzing cooks boiled for 0.5 to 3 hours, that the combined rosin reaches a maximum in 0.5 hour, though this size had a different appearance from the 3-hour size.

Early practice called for the use of neutral size, in which all the rosin was combined with soda, but recently sizes have contained more and more free rosin.   The permissible amount of free rosin varies with the method of handling the size; if it is added to the beater without first dissolving, the limit is about 35 per cent of the total rosin, and it is usually considerably lower.   If an emulsifying or dissolving apparatus is used the free rosin may safely go as high as 45 per cent with only sodium resinate to emulsify the free rosin.   With special emulsifying agents and apparatus, all the rosin may be in the free state.   The theoretical amount of sodium carbonate required to give a neutral solution with pure abietic acid is 17.5 per cent, but if this amount is used with commercial rosin, the size will still contain considerable free rosin, hence it is quite general to use even more than this.   With high-free-rosin sizes for use in emulsifying apparatus the amount of soda may go as low as 7 per cent of the rosin.

Freshly made neutral size is generally clear and dark in color, while free-rosin sizes may be clear and dark, or opaque and light colored. If a free-rosin size contains about 50 per cent of water and appreciable free soda, on cooling there will separate a dark, reddish brown liquid containing the excess of soda and some of the coloring matter of the rosin.   In the older methods of size making this separation was sometimes aided by adding a little common salt to the size, the idea being to remove dark coloring matter and improve the whiteness of the paper. It is doubtful whether this is worth while, since the dark liquor when acidified gives a precipitate which is only slightly grayish in color. The proportion of water in a size has an important influence on its consistency; at the end of the cook it should be sufficiently fluid to strain through a 60-mesh wire screen.   It is occasionally found that a size is too thick, but on adding water it becomes thicker instead of thinner. It is also frequently noticed that a size containing 30 per cent of water is thinner than one with 50 per cent, so a thick boil may indicate too much, rather than too little, water.

It is claimed that the clearer the size, the finer the dispersion. Wieger states that the optimum particle diameter lies between 2 and 10 microns.   Cobb et al.[13] and Nietzke[50] find that, below the limits of particle diameters which will bring on rosin or wax spots, coarse particles seem to size just as well as fine ones. Dennett and Libby[20] prepared

suspensions of pure abietic acid in gelatine solution and studied the effect on sizing, as shown by the Valley tester, of particle sizes between 226- and 688-mμ radius. It was found that above 350 mμ sizing was poorer and decreased sharply as the upper limit of the experiment was reached. " H " grade rosin in gelatine had 83 per cent of the sizing efficiency of abietic acid; a high-free-rosin size (80 per cent free rosin) had 88 per cent of its efficiency, and a nearly neutral size was 49 per cent as efficient.

Preparation of Wax Size. Paraffin is the wax most commonly used in wax sizes. It is not saponifiable and must be prepared for use by emulsifying it in water, thus obtaining a water dispersion of wax particles surrounded by a protective film which keeps them from re-uniting into a sold mass. The emulsifying agents used may be rosin size, casein, bentonite, emulsifying bases especially designed for dispersing paraffin wax, or sodium, triethanolamine, or ammonium soaps, such as ammonium linoleate. In general the ease of emulsifying the wax varies inversely as the interfacial tension between water and the mixture wax-plus-emulsifying base. Harkins and Zollman[25] state that if this interfacial tension is extremely low — 1 dyne or less — the emulsion can be formed spontaneously, with only a hand paddle for agitation. Emulsifying bases are available which are designed to make such emulsions, one of which, described by Cobb, Chamberlin, and Dombrow,[13] is made by mixing 4 parts of paraffin with 1 of base, melting, and adding the water in definite steps to insure proper emulsification by release of energy at the critical moment.

If the interfacial tension is higher than 1 dyne, work has to be done on the system according to the equation of Thomas:[76]

$$W = T\Delta S$$

where W = work.

T = interfacial tension.

ΔS = increase in surface of oil due to emulsification into fine droplets.

Since the original surface of the oil is negligible, the total surface which results when wax or oil is emulsified in water equals ΔS, and is related to the total volume of oil V and the diameter of the emulsified oil droplets d as

$$\Delta S = \frac{6V}{d}$$

$$W = \frac{6TV}{d}$$

The equation shows that the finer the emulsified oil droplets become, and the greater the interfacial tension between the oil and the water phase, the greater the power required to effect emulsification by mechanical means.

While the calculated amount of energy is not very high, the efficiency of dispersing equipment is quite low, so an appreciable expenditure of energy is necessary for emulsification, even when the interfacial tension, T, is as low as 4 dynes. In one important patented process[49,50] the wax and rosin are emulsified together by production of rosin soap in situ, followed by rolling in a special colloid mill designed for the purpose. In this case the rosin and wax form one entity, and some feel that because of this preblending the behavior is better on the machine. On the other hand, some mills prefer to use wax and rosin separately in order to enjoy flexibility in the rosin-wax ratios.

Special Sizes. Special sizes may be considered as modifications of rosin or wax sizes. In Bennett wax-rosin size, saponified rosin is the chief emulsifying agent. Delthirna size is a fully saponified rosin, made by circulating a dilute solution of caustic soda through pipes containing rosin in coarse lumps.

Bewoid size[85,86] is nearly all free rosin with a little casein as the emulsifying agent. Dry sizes are cooked in the regular manner, fully saponified, and dried until they contain practically no water. They may be added dry directly to the beater. . Nopco size is a base specially designed for emulsifying paraffin wax by the addition of water.

Montan and carnauba wax sizes consist of saponified waxes which may be used to harden paraffin sizing films.

Paracol is an all-wax size prepared in emulsion form.

Solvent sizing was developed by Minton[48] and based on the work of Arledter,[1] who, in 1896, sized paper with rosin dissolved in alcohol. It consists in dissolving rosin in carbon tetrachloride or other non-flammable solvent and applying it to the dry web of paper at the end of the machine. Commercial success depends on solvent recovery in a Minton vacuum drier or similar apparatus.

A review of special sizes, some of which, however, are not of commercial importance, has been made by DeCew.[19]

General Nature of Sizing Agents and the Sizing Process. Those familiar with the molecular orientation theory of Langmuir will immediately see that all water-dispersed sizing agents consist of two parts: (*a*) the polar, water-soluble portion; and (*b*) the non-polar, water-insoluble, water-repellent portion.

In rosin size, or sodium resinate, the water-soluble portion consists of the sodium ion, the presence of which confers a certain degree of

solubility upon the entire rosin molecule. The water-repellent portion consists of the hydrocarbon end of the abietic acid molecule.

Wax emulsions also have a water-soluble end, consisting of the polar part of the emulsifying agent, which is wholly or partially soluble in water. Here, too, the water-repellent portion consists of the hydrocarbon end of the wax molecules.

The beater sizing process consists of precipitating the sizing agents upon the fiber in such a way that they will be firmly fastened upon the fiber, probably with polar end bound to the fiber, and the water-repellent end sticking out to raise the contact angle of the fiber against water. This orientation has been discussed by Cobb,[11] Wooley,[37] and Kumler,[38] and is believed to follow the conclusions of Langmuir[39] with regard to the orientation of molecules. Cobb[12] has calculated that 2 per cent of rosin will give an oriented film 40 molecules deep, if the film were equi-thick and continuous over the fiber's outer surface of 0.2 square meter per gram.

Addition of Size to the Beater. In a system uncomplicated by carbonates or other desizing fillers, size is generally added to the beater after the fibrous stock and filler, but before the alum. If rosin size contains less than 35 per cent of free rosin it may be added in 60–70 per cent concentration directly to the beater, or it may first be dissolved in luke-warm water. Hot water should never be used as it causes the free rosin to collect in lumps which make spots in the paper. So far as sizing efficiency goes there is probably not much to choose between adding directly to the beater or dissolving, but as the dissolved size may be strained through cloth or allowed to settle, it is preferable from the standpoint of cleanliness.

High-free-rosin sizes must be diluted before adding to the beater, and some form of emulsifying apparatus should be used to make the diluted emulsion of free rosin so fine that no particles will settle out. The emusifier is practically a steam injector which sprays the hot size suddenly into a large body of cold water. This prevents the free rosin from collecting in flakes and gives very fine particles in suspension. Some emulsifiers can be regulated to give emulsions ranging from a milky suspension of comparatively coarse particles to a semi-transparent brownish one in which the particles may be as small as 0.1 micron in diameter. The upper limit for a satisfactory dispersion by this means is a rosin size containing 2 to 3 per cent of rosin. The claims made for the process are more uniform size, less dirt, and cheaper and better sizing because of complete dispersion.

Kamm[30] has devised a method for diluting high-free-rosin sizes without an emulsifier. The rosin is cooked with caustic soda until the

solution is clear and homogeneous, and 4–5 parts of hot water are then added. The whole is heated nearly to the boiling point, and when it again becomes clear it is poured into 45 parts of cold water. This gives a practically clear, 2 per cent rosin solution.

Wax sizes when purchased contain as much as 70 per cent solids, and when prepared in the mill run from 20 to 50 per cent. If correctly made they may be readily diluted with water at about 100° F., and the more stable the size, the further the dilution may be carried. Wax sizes are added to the beater in dilutions ranging from heavy size down to 2 per cent.

The formation and characteristics of clear and opaque emulsions of rosin have been discussed by vonPossanner.[50] Kent[31] states that the color of opaque emulsions varies directly with the free rosin. Sieber[68] claims that an aqueous solution containing sodium soap and free rosin is clear only at concentrations of 4. to 5 per cent and within narrow temperature ranges.

Precipitation of Sizes. The mere presence of rosin or wax size in the stock does not mean that the paper will be sized; much of the art of sizing consists in precipitating the size on the fiber in such a way that the paper on drying will be water-resistant. In practice this is successfully done by precipitation with alum, usually over the pH range 4.2 to 5.5. The retention of rosin varies from 35 to 65 per cent.

Researches by Wurster in 1878 led him to conclude that the prime sizing agent was free rosin thrown down by the alum, and on the basis of these, the earliest experiments on record, much stress has been laid on the use of sizes high in free rosin. There is still much discussion, however, regarding the function of alum in precipitating size, and the reaction between the two has never been definitely ascertained. There is a marked lack of agreement as to the reaction when the two combine alone, and the presence of cellulose still further complicates it because of its ash constituents and the resulting base exchange.

Precipitation of free rosin cannot be the only function of alum, otherwise acids, which also throw down free rosin, could replace alum entirely; this they cannot do. Neither can the precipitation of basic aluminum resinate be its only function, contrary to the conclusions of Schutz and Klauditz,[62] for theoretically 0.3 part of alum will precipitate 1 part of rosin, but in mill practice 1 to 2 parts of alum are needed for every part of rosin. Practical experience has also shown that, other things being equal, a pound of rosin has the same sizing power, whether used as neutral size or one containing 30 per cent of free rosin.

Ivanoff[28] reported that at a dilution of 0.5 gram of rosin per liter as much as 95 per cent of the rosin was free, and concluded that at

beater dilution practically all of it would be in that state. Bialkowsky,[5] however, contradicts Ivanoff and finds rosin soaps present at dilutions of 0.324 to 3.24 grams per liter in the beater. With neutral sodium resinate he finds only 0.5 per cent hydrolysis in a solution of 3.24 grams per liter at 30° C., while in one of 1.08 grams per liter at 56° C. only 4.3 per cent was hydrolyzed. These results are in close agreement with the data of Beedle and Bolam.[2]

Bialkowsky also finds the hydrolysis greater in the presence of pulps, being forced in proportion to their tendency to remove alkali from dilute alkaline solutions. He assumes that the abietic acid is liberated in very fine condition by adsorption of alkali by the pulp; and that this free rosin can be adsorbed or held mechanically by the fibers. He finds that the relative degree of hydrolysis of resinate by different pulps agrees with their relative ease of sizing. His results were confirmed by Robinson.[59]

Rowland[60] found that protein matter suspended in solutions of alkali resinates abstracts the alkali and sets free the rosin in particles of colloidal dimensions. The action may be hastened by warming and by the addition of very small quantities of dilute acidic buffer mixtures, and is indicated by increasing turbidity in the liquid. This is the basis of the so-called Prosize process in which soybean protein is used.

Glue has been extensively used as a protective colloid in rosin size, the amount varying from 1 to 20 per cent of the weight of the rosin.

Though acids and acid salts of divalent metals will precipitate sizing materials, only trivalent salts, such as aluminum or ferric sulfates, are used to fix the sizing agent on the fiber. Other precipitants which have been tried at times include sulfuric, acetic, and carbonic acids, acid sodium sulfate, zinc and magnesium sulfates, and calcium chloride, but none is as effective as the trivalent aluminum salts. None of the precipitants having an alkaline base, such as copper, lead, or zinc, will give good results, nor will the salts of the alkaline earths, such as magnesium sulfate or calcium chloride.[22,56]

Sizing and the Electric Charge. Thiriet and Delcroix[75] were among the first to study the optimum pH for sizing, and proposed the theory that, over a range of 4.5 to 5.0, cellulose and rosin have electric charges of opposite sign, so that sizing is possible by mutual attraction. They believed that outside this range the electrolyte in solution was too acid or too basic, so that rosin and cellulose were charged similarly and sizing was impossible.

That sizing offers a problem is due to the fact that most organic colloids such as cellulose, waxes, and rosin have a negative potential

with respect to water, thus repelling one another in the presence of water.

In discussing the electric potential of cellulose Stamm[70] explains that solids suspended in water assume an electric charge with respect to the liquid as a result of selective adsorption of ions.

According to Briggs[8] the negative potential of cellulose is increased by monovalent cations at low concentrations, remains about the same in the presence of divalent cations, but is decreased markedly by aluminum. It becomes zero at relatively high concentration of aluminum ion, and positive at still higher concentrations. Sizing is thus successfully accomplished by the reaction of size with trivalent aluminum under conditions which undoubtedly render the charge on cellulose particles positive in the presence of water, but the role of alum cannot be simply that of rendering the fibers positive, for thorium with a valence of 4, in the form of thorium sulfate, renders fibers still more positive, yet it does not size paper as does alum.

The change in charge on organic colloids brought about by aluminum has been discussed in a paper by Setter and Mattson[64] on the electrophoretic effect of aluminum on the coagulation of soil colloids; the coagulation strikingly resembles the precipitation of sizing materials by alum. This study shows the cation exchange capacity and the conditions under which the organic soil complex will lose its negative charge. When the amount of aluminum salt is very small, enough acid to make the pH very *low* must be used before the soil complex will lose its negative charge, become positive, and start moving toward the opposite or negative pole. With *large* quantities of aluminum chloride the soil complex will become positive and start traveling toward the negative pole at a *high* pH, as high as 6.85.

This tendency for organic soil colloids to become positive at different pH's is in remarkably close accord with the results of Healy and Dyer,[26] who worked with fibers, rosin, alum, and sodium aluminate, and found that an effective sizing precipitate could be obtained at high pH if the total alumina concentration was kept high by means of aluminate combinations.

Miller[46] believes that the aluminum ion and not alum floc is of primary importance in the flocculation of rosin size, but Shnyparkov[67] thinks that aluminum hydroxide, and not aluminum ions, is responsible for sizing, because he believes that the former is adsorbed by cellulose and the latter not. Khinchin[32] concludes that cellulose is not an amphoteric substance, the apparent amphoteric properties being traced to adsorbed impurities. He states that aluminum is so adsorbed by base exchange with impurities, especially between pH 4.5 and 5.0, being

retarded at lower pH and completely inhibited at higher values. Sutermeister[74] finds that the amount of aluminum adsorbed by fiber is independent of the aluminum concentration.

Blodgett and Langmuir[39] have found that when fatty acids are placed on water or solutions of monovalent and bivalent salts a fluid film is formed, but that when laid on solutions of aluminum salts the resulting films are rigid solids. It might be believed that alum functions in sizing by changing the film of rosin which would flux on the dryers into a rigid film, which will prevent its penetrating into the fibers where its effect would be lost. This cannot be the real function of the alum, because after the effect of solvent sizing is lost, an alum soak will restore it; and alum cannot withdraw rosin from the interior of the fiber once it has penetrated.

Thomas,[77] in a summary of the work of Stiasny,[71] Werner,[84] Bjerrum,[6] and Thomas himself,[78] present the picture of alum functioning by binding cellulose fibers coordinately through secondary valences as aluminocellulose unit micelles which react with rosin or wax emulsions, binding them to the fibers. This is substantiated by the fact that sulfates, nitrates, chlorides, and acetates of aluminum will size paper, and these anions are, according to Thomas, the least strongly coordinated to aluminum and would be the easiest to replace with cellulose, thereby making the cellulose part of a positive complex. Oxalates, succinates, and tartrates of aluminum will not size paper; and, as these anions are so strongly bound to aluminum that it is extremely difficult to replace them with inorganic anions such as sulfates, it may be assumed that it is impossible to replace them with cellulose.

Whatever its reactions with size may be, the specific function of alum is to affix and orient the rosin or wax on the fiber. It is possible that, under the varying conditions prevalent throughout the industry, the sizing precipitate may consist of varying mixtures of free rosin and aluminum resinate. Certainly free wax is present in the wax-size precipitate. Since any of these precipitates, when properly oriented by alum, will raise the contact angle of fiber against water, it is also possible that the exact composition of the sizing precipitate may vary without materially affecting the sizing of the sheet.

Addition of Alum in the Beater. Some light on the role of aluminum in sizing paper may be obtained by considering the quantities of alum used in practice. With a neutral size, 0.202 pound of alum (17 per cent Al_2O_3) is sufficient to precipitate each pound of rosin, while with a 31 per cent free-rosin size the figure found by titration is 0.201 pound. In actual operations these proportions are never even approximated, for if they are the paper is very slack sized, which indicates the

necessity of having an excess of alum over the amount necessary to cause mere precipitation of the rosin. Experience has shown that the ratio of alum to rosin should not fall much below 1.5 to 1 if good sizing is to be expected.

The value of an alum is generally considered to be in proportion to the amount of alumina which it contains, though this does not indicate its size-precipitating power, since impurities such as zinc salts and free acid also cause precipitation of the rosin.

The amount of alum used depends on a number of factors besides the amount of size employed; hard water and an increase in the temperature of the stock in the beater necessitate additional alum. The quantity to use is generally determined by experience rather than by scientific observation, and it is always largely in excess of that necessary to precipitate the size and usually of that necessary to effect good sizing. For a 1000-pound beater between 12 and 30 pounds of alum would ordinarily be employed in sizing, and even more for very hard-sized papers.

The method of adding the alum has some influence on the results obtained; it is usually best to have the size thoroughly mixed with the stock before furnishing the alum, but some mills reverse these operations and add the alum first. With some water supplies it is customary to add part of the alum to give the water a pH of 4.5 to 5.5, before the size is in, and then add the rest of the alum afterwards, on the theory that the combination of size with lime salts will be prevented by the stronger activity of the alum. Experience has shown that, even if sufficient calcium chloride is present to combine with all the size, subsequent addition of alum breaks down this combination and gives fully as good sizing as in the entire absence of this salt. This division of alum is said to reduce frothing, and on this basis may be justified.

Minor[47] has pointed out that, once fibers become alkaline because the size is added first, subsequent acidification by alum does not penetrate them completely, and later on the interior alkalinity asserts itself, perhaps even resulting in a desizing action. This difficulty is eliminated[18] by means of a divided alum furnish.

The extent to which the alum may be reduced is limited by the difficulty of the stock sticking to the couch and presses of the paper machine. Trials on a book paper machine showed that sticking occurred if the ratio dropped to 1.2 alum to 1 rosin, but that it ran safely if the ratio was 1.5 to 1. All this leads to the conclusion that the role of alum is not just to precipitate rosin, but to fix it on the fibers and to orient it in such a way that it will repel water and will not stick to the machine. Schwalbe[63] even assumes that each particle of rosin

must be surrounded by an envelope of aluminum hydrate to protect it from the action of air and light and keep the sizing from deteriorating.

Since a solution of rosin, wax, or aluminum resinate in organic solvents will size paper temporarily after evaporation of the solvent, aluminum is not necessary in the sizing film; but when sizing is carried out in aqueous solutions, aluminum seems necessary for the orientation or fixing of the film on the fibers. Oeman[52] found that an ether solution of aluminum resinate was capable of sizing paper, but though a suspension of neutral aluminum resinate in water had sizing properties, it gave results inferior to those obtained in the presence of alum or acid.

Microscopic examination of poorly sized papers by Lee[40] showed much of the rosin in large granules with a smaller part in much finer grains. On paper hard-sized to writing ink, the rosin was finely divided and well distributed. Rosin deposited from solution is found in scattered masses on the fiber, resembling that which occurs when the size is precipitated by sulfuric acid instead of alum, and yielding sizing which is not permanent. In no paper did Lee find a distinct, continuous layer surrounding the fibers, though the rosin particles might be so closely packed that they gave the effect of a continuous film. It must be borne in mind that submicroscopic particles of rosin may exist and may likewise pack tightly together, even though the microscope cannot detect them. A monomolecular layer of sizing material can raise the contact angle of paper fiber against water. This is also effected by large flakes of rosin or wax if they are not too far apart, so the contact-angle theory does not necessarily call for a continuous film upon the fibers.

The control of sizing is aided by pH indicators, bromcresol green and chlorphenol red being particularly useful for this purpose. Shaw[65] found the maximum precipitation of alumina at a pH of 5.0 to 5.5, and that alum used in excess of that required to give this value had no favorable effect on the sizing of the paper. Lorenz[43] and Bennett, Ltd.,[4] both point out that sizing is best if the pH is high, 6.5 to 7.5, before the size and alum are added.

It is frequently found that the sizing values of the paper vary widely, even when the pH of the stock going to the paper machine is constant, and conversely that the sizing in the paper is often the same when the pH values of the stock are very different.

When using the pH indicators to follow alum economy, the alum should be added gradually through the cycle 6.5, 6.0, 5.5, until the desired low pH is reached. It must be remembered that pH is expressed on the logarithmic basis, so that it changes only 0.3 unit in value when the hydrogen ion doubles in concentration. This goes far

toward explaining the observed fact that, when the weights of rosin and alum furnished were equal, the pH was 4.6, but that using twice or three times as much alum dropped the pH of the beater to only 4.4 and 4.2 respectively. Booth[7] points out the desirability of departing from the logarithmic expression of acidity, and stating the actual parts of free acid present.

Quantities of Size. The amount of rosin used in sizing paper varies greatly; in some grades it may drop as low as 0.25 per cent of the stock furnished, while in hard-sized papers it may amount to 2 per cent on regular grades and 4, 6, or even 8 per cent on specialties.

Some fibers are easier to size than others. Wieger[86] arranges the pulps as follows, the easiest to size being given first.

1. Unbleached kraft.
2. Brown steamed groundwood.
3. Bleached kraft.
4. Unbleached sulfite.
5. Bleached sulfite.
6. Rope.
7. White groundwood.
8. Esparto.
9. Rag and alpha pulps.
10. Brown and white groundwood from green wood.
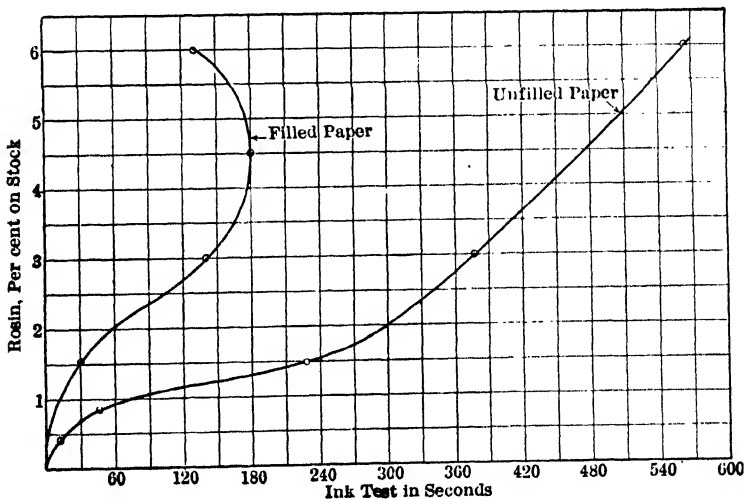
Fig. 45.

Sizing increases with the quantity of sizing agent used, but the increase is not proportional to the increase in rosin throughout the entire range, the effect being greatest between 0.75 and 1.5 per cent.

The sizing of unfilled paper and that containing 18 per cent of ash is illustrated in Fig. 45. This shows the difficulty of sizing filled stock

and the waste in going beyond the amount of size which will give maximum sizing.

The ratio of wax to rosin size may differ over wide limits; 1.5 rosin to 0.5 wax is common practice, but the ratio may be varied to suit the requirements of the particular product. According to Nietzke the maximum sizing value is obtained when the wax amounts to not over 20 per cent of the total dry sizing material. A 100 per cent wax size is likely to give a soft sheet and lower the bursting strength.

The amounts of size used in various grades of paper have been listed as follows:[10]

PAPER	% SIZE	PAPER	% SIZE
News	0 –0.5	Wrapping	2.5–3.5
Book	0 –2.0	Patent coated board	1.5–2.0
Writing	2 –3	Wallboard	2.0–5.0
Bags	0 –4	Blueprint	3.0–5.0
Kraft	1.5–2.5	Container board	3.0–5.0

Sizing Troubles. Trouble in sizing frequently occurs in hot weather and particularly in beaters where the stock tends to become heated. This is probably due to the rosin particles uniting to form larger masses which do not cover the fibers well.

Water containing calcium bicarbonate, or the presence of calcium carbonate in the stock, is particularly bad for sizing. Calcium hydroxide is also very harmful,[73] but calcium sulfate and chloride have practically no influence on sizing, even as much as 5 per cent of $CaCl_2$ being harmless, though more than enough to precipitate all the size. It appears that the alum reacts with the precipitate of calcium resinate to form free rosin or compounds which are capable of sizing. This is fortunate, for the bleached fiber used often carries enough calcium chloride from exhausted bleach residues to precipitate all the size used.

Other disturbing factors are the soluble matters washed into the water supply by heavy rains, the presence of much filler, or of acid in incompletely washed sulfite fiber.

In the presence of carbonates, wax sizing is usually employed on the theory that the carbonate cannot react with paraffin to spoil the sizing and that when wax is once precipitated it will not redissolve or re-emulsify at the high pH maintained with calcium carbonate filled papers. While both these premises are undoubtedly true, the fact remains that at a pH of 6.8 wax-sized papers are not always fully sized — often not nearly so well sized as they would be at a pH of 5.5.

To overcome many of the difficulties due to hot weather or presence of carbonates, many observers recommend that the size be added to the stock as late as possible. The patent literature contains numerous

references[18, 58] to the importance of keeping the size in contact with the carbonate-containing stock as short a time as possible before forming the sheet. Minor[47] has called attention to the fact that, if fibers are first acidified with alum, the acidity will remain inside the fiber despite subsequent treatment with alkaline material. Hence some recommend that the order of sizing filled stock should be: (a) alum added to the beater to fix the pH permanently low; (b) rosin to form the sizing complex, added wherever there is adequate agitation, from the beater to the machine chest; and (c) calcium carbonate filler added at the last possible minute to desize the stock as little as possible before the web is formed and dried.

The difficulty of sizing in the presence of calcium carbonate is largely because the carbonate starts to decompose below a pH of 6.8, while paper is not well sized at that point. A pH of less than 6.8 not only destroys calcium carbonate but also produces CO_2 gas which hurts sheet formation. To overcome such difficulties Kress and Johnson[36] propose the presizing of the calcium carbonate itself before adding it to the beater.

One of the most annoying difficulties is fugitive sizing; in this trouble, sizing is adequate at the machine, but the paper becomes unsized after periods varying from 24 hours to 6 months. Apparently the desizing action of calcium carbonate can proceed after the drying operation, especially in rolls of paper which remain warm. Wax sizing is not so readily affected in this way as rosin sizing, indicating that the undesirable reaction occurs between calcium carbonate and the rosin-sizing complex. Other factors as yet unknown may also cause sizing to be fugitive, for the effect is also experienced with groundwood sheets which contain no calcium carbonate or alkaline filler.

Defective sizing may also be caused by calendering, which has been found to reduce the resistance to ink from 6 to 40 per cent. Other factors which may cause defective sizing are too much filler, improper proportion of alum, and poorly cooked size. According to Turner,[79] the length of time the alum acts may influence sizing, a long time being harmful. Free acid has the same effect as long time, and white water, in which alum accumulates, may cause trouble because of its hydrolysis into acid. He found rag pulp harder to size than sulfite, and unbleached fibers and groundwood harder than bleached stock. Fir does not size as well as spruce, while increasing amounts of oxycellulose cause the fiber to size more easily.

Machine Effects. Sizing is not completed until the paper has passed over the dryers, and the machine conditions have great influence on the results. Comparative sizing tests of hand sheets made from stock

going on the machine, and paper formed on the machine, will indicate whether the machine conditions are handicapping the size. Harmful conditions may include too rapid a rate of extraction of water, carrying out much size; improper drying; crushing of the sizing film on the calenders; and extraction of size by hot water in the water boxes. Since the best of sizing materials and precipitation practice may be defeated by wrong machine conditions, investigation of sizing trouble should start at the machine.

No thorough work on machine conditions has been carried out, although some authors have ventured an opinion on certain phases. The best dryer conditions are said to be moderate steam pressure on the first dryer, increasing to a maximum at about the middle of the bank, and again decreasing toward the calenders. This warms the paper gradually but permits it to reach a high temperature before the moisture is driven off. Klemm[35] believes this essential to good sizing and states that, if the first dryers are too hot, the sudden escape of steam may destroy the sizing film, while, if the paper becomes too dry before the proper temperature is reached, the desirable chemical reactions do not occur and the sizing is poor. He believes that the temperature should reach 70° to 80° C. before the moisture falls below 50 per cent, so that the sizing film will sinter, before it shrinks so much that gaps will form in it. Oeman,[53] in contrast, feels that paper should *not* reach 73° C. until the moisture drops to less than 55 per cent. He states that, if rosin-sized paper containing 45 per cent of moisture or more is warmed to 75° C., the degree of sizing is greatly decreased or even destroyed.

The fact that moist heat is a requisite of good sizing is borne out by the observation that slack-sized paper may often be greatly improved by exposing it to steam even at as low a temperature as 100° C.

Minor[47] and also Klemm[35] state that paper taken from the machine before the dryers and air dried is usually not well sized. Klemm believes that two or three dryers on the machine are responsible for the major part of the drying, and that sizing takes place at the point of major shrinkage.

Experiments on the drying of sized stock taken from the first press of a paper machine were made on a steam-heated cylinder against which the sheets were pressed by means of a felt. Over the range of 100° to 152° C. in the dryer the maximum sizing occurred at 106° to 112°. If the paper were alternately pressed against the cylinder and removed, as in passing over the dryers of a paper machine, the sizing was only one-third to one-half as strong as when held against the dryer continuously.

Turner[70] claims that, with very small amounts of rosin, slow drying at low temperatures gives the best results; with increasing rosin there is a range where it seems to make little difference whether the paper is dried in the air at low temperature or on the dryers; but above a certain percentage of rosin the effect of the heat of the dryers is beneficial.

The relation between the drying conditions and the sizing of the sheet has apparently been given little study, but it must be investigated much more carefully before it will be possible to say that the best conditions for sizing are maintained.

Effect of Sunlight on Sizing. If rosin-sized paper is exposed to sunlight the sizing is destroyed and the paper becomes absorbent. This is probably due to the formation of the friable substance insoluble in petroleum ether, previously mentioned. The use of a small amount of tannin with the size is said to retard this change, but it is likely to cause bad discoloration of the stock in the beaters. Zhereboff[89] found the action of sunlight on rosin-sized papers rapid enough to show in 10 days, while after 1.5 to 2 months all papers became slack sized, and after 6 months they were as though unsized. The violet, blue, and yellow rays are most effective in destroying sizing, red and green having little influence. Similar experiments by others showed a very marked drop in resistance to writing ink after exposure to sunlight in a south window for 3 days. A paper in which acid was used instead of alum became totally unsized in this time, while those in which alum was used lost on an average about half their ink resistance.

Ivanoff[29] has studied the destruction of sizing by light and its restoration by heat, and has shown that the sizing quality in papers is dependent upon the electrical conditions of the paper, the sizing materials, and the ink.

Sizing and Paper Permanence. It has been thought that rosin in paper causes deterioration of the fibers, according to the amount present. Shaw and O'Leary,[66] however, have found that rosin alone may have negligible effects upon permanence; the destructive effect of sizing comes chiefly from the acidity caused by the alum. They show that, the higher the pH at which paper is sized, the less acid appears in the finished sheet, and the more permanent the paper. These important findings are causing mills to turn more and more to the use of alkaline fillers as the simplest method of reducing free acidity in the finished sheet. For a mill making a product which need not be water resistant the use of carbonate filler causes no serious difficulty, but for writing papers or others in which a fairly hard sizing is demanded its use offers a truly major problem.

The yellowing of paper has been variously ascribed to rosin, to soaplike compounds of rosin with iron, or to bleach residues. Zschoke[90] concluded that wood-free paper with not over 1 per cent of rosin would not become yellow, while Klason[33] believed that papers properly sized with rosin would not be injured within 60 years.

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CHAPTER XI

LOADING AND FILLING

A. E. H. FAIR

Paper loading has been practiced for years and was formerly considered to indicate adulteration, but the modern conception that the use of loadings makes papers more suitable for particular uses justifies the term " fillers " and the abandonment of the idea of adulteration. The use of fillers is very general, and some mineral content is present in nearly all grades except a few for special purposes. This increase in their use has coincided with developments in the graphic arts, paper making and converting, and as the demands on paper increased, those on fillers became more exacting and many new ones were introduced. (Fillers in paper improve printing qualities by increasing its opacity, preventing " show-through " and " strike-through," and giving more " body " to the sheet. They improve the " feel," and they give a better finish on calendering and that smooth, polished surface which is essential to fine printing. Too much filler causes low strength, extreme softness, and dusting; too little tends to give a hard sheet and a poor surface. The correct amount, if not properly anchored in the sheet, will cause dusting.)

Fillers, generally, tend to increase weight more than bulk in paper, and it was difficult to produce high-color, opaque " featherweights " until the advent of new fillers which gave high opacity with low ash content. By supercalendering a heavily filled sheet an imitation coated paper can be obtained, but if large amounts are used the strength of the sheet is considerably decreased, so the strength demanded limits the possible filler use. If the filler must exceed this limit, changes must be made in the fiber furnish and treatment, but if the need for high filler depends on that for high opacity a blend of new and old types of fillers may give the desired opacity with a low ash and no fiber change. Fillers also affect the sizing of the paper; up to 13–15 per cent of non-alkaline filler has little effect, but more than this decreases sizing appreciably with increasing filler.

Filling Materials. Among the older fillers are china clay, talc, calcium sulfates, barium compounds, and precipitated chalk; of these, china clay and chalk are the only ones used extensively. Clay is probably the most generally used of any filler.

323

The new type fillers include titanium dioxide and its compound pigments; zinc sulfide, alone or as lithopones and titanated lithopones; and modern forms of calcium carbonate. These are important because of their high whiteness and their ability to impart higher opacity with
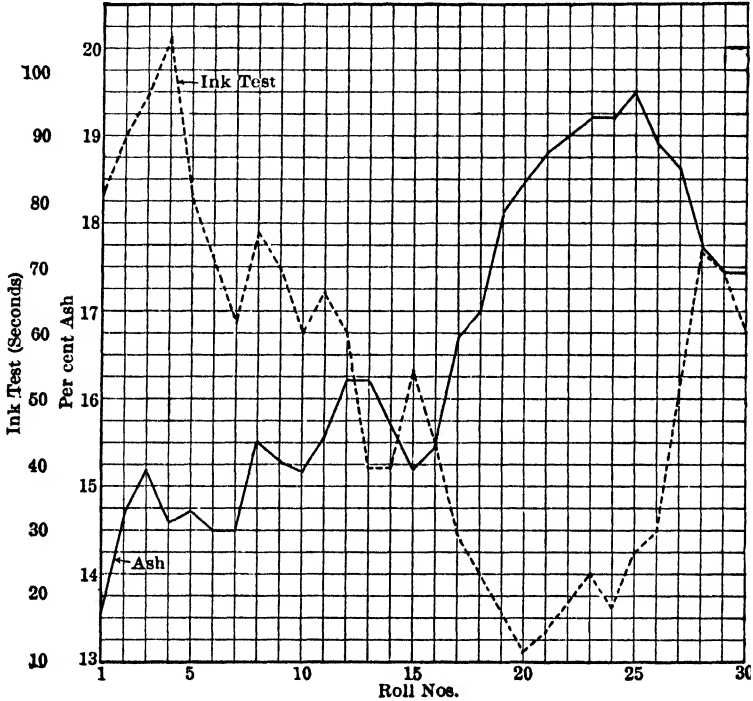
FIG. 46.   EFFECT OF FILLER ON SIZING.

lower ash content. Calcium carbonate and precipitated chalk are the same chemically, but the new products are made in ways which give finer particle size, and they have taken an important place in magazine and book papers.

The qualities to consider in judging a filler include color, fineness, absence of grit and foreign matter, solubility, specific gravity, and chemical composition. High whiteness is more important than ever, and freedom from grit is usually assured by modern methods in pigment production; a filler must rate highly on both points to stay on the market. High solubility under use conditions tends to cause high filler loss. High specific gravity also results in high loss, increased two-sidedness, and reduction in bulk. Chemical composition, as a check on shipments, is of little value, but it must be known, so that its relation to the dyes and other chemicals used may be ascertained, and

to permit ash determinations to be converted to filler content. Fineness of particle size is much more important than formerly because of its effect on opacity, retention, and finish imparted to the paper; the index of refraction of a pigment should also be known because of its influence on opacity. Modern methods of filler manufacture are such as practically to guarantee a number of these important properties, and so the choice of kind and source often depends on the price and the result desired.

TABLE 54

REFRACTIVE INDEX AND SPECIFIC GRAVITY

Material	Refractive Index	Specific Gravity	Material	Refractive Index	Specific Gravity
Air..............	1.00	....	Calcium sulfate..	1.58	2.30
Water...........	1.33	1.00	Barium sulfate..	1.65	4.45
Gypsum..........	1.52	2.36	Titanox B (25%)	1.90	4.30
Cellulose.........	1.53	....	Lithopone.......	2.00	4.30
Clay.............	1.55	2.60	Zinc oxide.......	2.01	5.95
Calcium carbonate	1.56	2.70	Zinc sulfide......	2.37	4.00
Asbestine.........	1.56	2.85	Titanox A (TiO₂).	2.55	3.90
Talc.............	1.57	2.77			

Formerly all fillers were added dry to the beater; this was followed by mixing with water and adding in slurry form, to facilitate handling, and screening for removal of lumps and grit. It has been shown that fillers in the beater greatly increase the wear on the knives, and when they are so used the ash content of the paper cannot be altered quickly.

The next step was adding the filler slurries to the white water system; then as the paper machine underwent changes involving suction couch rolls and presses, higher speeds, etc., other methods of addition were sought. These were first suggested in special sizing processes[25,20,13,9] and were followed by various methods of adding the filler directly to the sheet on the wire, either at or before the dandy roll,[15,16] and still more recently by methods for coating the paper on the paper machine. (See Chapter XIII.) While beater addition of filler is still widely practiced, it is not so universal as formerly and the trend is definitely toward machine application because of its greater flexibility, better retention, and the growing demand for special surfaces and finishes.

Clay. China clay is a soft, friable, sectile, white mineral, showing irregularly shaped particles under the microscope and having only moderate plasticity when mixed with water. Its specific gravity is variously given as 2.4 to 2.86; English clays have been found to range

from 2.57 to 2.63, while Georgia and Alabama clays were found by Weigel[24] to vary from 2.501 to 2.636, with an average of 2.59 for 40 samples. Its weight per cubic foot, as usually received with about 7.5 per cent of moisture, is about 53 pounds when the fine material is run loosely into the container, to 84 pounds when the clay is tamped in hard.

China clay, or kaolin, is formed by the weathering of igneous rocks (feldspars), and the presence of mica indicates its granitic origin. There are two types of clay, residual, which remains overlying the rock from which it was formed, and sedimentary, which have been carried to a distance by eroding influences and deposited from the water which carried them.

There are many clay deposits throughout the world, but most are too impure for use in the paper industry. Good grades are found in England, France, Bohemia, and the United States. Formerly most of the filler and coating clay used in American mills was of English origin, but more recently the United States clays have been greatly improved and have replaced English clays to a considerable extent. This trend is shown by the imports of kaolins for all purposes, which averaged 329,014 tons per year in 1925–1929, but only 115,351 tons in 1937–1938. Domestic kaolins for these same years averaged 453,618 and 663,668 tons.[21] It is not possible to subdivide the imported kaolins according to uses, but over half of the domestic production went into paper.

There are several ways of preparing clay for market, but in all the first step is the removal of the overburden and the stained top clay. Sedimentary clays are sometimes pure enough so that pulverizing and air floating the dried clay will give a fairly satisfactory product at low cost, though it is bulkier and fluffier than other types.

The more common method, especially in England, is to wash the clay from the deposit by streams of water, into a pit where the coarse sand settles out and is removed. From the pit the clay and water pass through channels, termed " drags " or " micas," which take out fine sand and mica, and then into large settling pits where the clay collects and the comparatively clear water is drawn off. When sufficient clay has collected it is dug out and dried in long kilns having longitudinal flues beneath the floor through which hot gases pass. The drying time is from 1 day at the furnace end to 3 to 7 days in the cooler sections. The fine clay is sometimes separated from its water suspension by filter presses, and an electrolytic method of purification and separation has been proposed which is claimed to give a product perfectly free from grit and much drier than that from filter presses.

The most recently developed method of refining clays involves the separation of the slurry into fractions by means of centrifuges. This

is capable of producing very fine clay for coating purposes as well as a coarser product for filler use; it results in a greatly improved color due to high impurity removal, but its cost is high.

For filler purposes, clay processed by the older method of water washing seems to give the best all-round results, considering color, retention, opacity, finish, and wear on machine clothing. The slow processes of flotation, settling, and decantation give more uniformity and better impurity removal than the more rapid methods, some of which do not take out impurities but merely subdivide them finely enough to give a satisfactory screen test.

Chemically, clay is a mixture of hydrated silicates of alumina with particles of quartz, mica, and feldspar as impurities. Its composition is approximately $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, or 14 per cent H_2O, 44 per cent SiO_2, and 42 per cent Al_2O_3. Mechanically held water may be driven out of clay by drying at 100° C. and the clay will regain its plasticity on wetting, but if the chemically combined water is driven off at a red heat its valuable properties as a filler are lost. Moisture in English clays may run up to 12 per cent, but domestic clays usually contain from 2 to 5 per cent. It is not well to have clay too dry, as it causes loss in handling bulk shipments and the dust is bad from a hygienic standpoint. Because of this loss on ignition the ash as determined in paper, and neglecting that from fibers, alum, etc., must be divided by 0.88 to convert it to the approximate amount of English clay, or by 0.865 if American clay was used. Air-dry clay contains a small amount of moisture, usually less than 1 per cent, which is driven off on drying at 100° C., but regained on exposure to air.

The analyses[15] of Table 55 give the composition of two domestic and two foreign clays; the domestic samples were from the same mine, but A had been washed only, while B had been chemically treated, bleached, and washed.

TABLE 55

Constituents	Foreign Clay		Domestic Clay	
	No. 1	Medium	A	B
	%	%	%	%
Silica (SiO_2).....................	46.7	46.2	44.4	44.3
Iron oxide (Fe_2O_3)...............	0.7	1.0	0.4	0.4
Alumina (Al_2O_3).................	37.5	37.6	39.8	41.0
Calcium oxide (CaO).............	Trace	Trace	Trace	Trace
Magnesium oxide (MgO)..........	0.3	0.5	0.5	0.1
Loss at 110° C. (2 hours)..........	0.4	0.3	0.6	0.4
Further loss on ignition...........	12.4	12.5	13.7	14.0
Specific gravity.................	2.71	2.75	2.67	2.70

These analyses make no mention of titanium dioxide, which is usually present in American clays, though less often in English. Weigel found the TiO_2 in the domestic clays which he examined to vary from a trace to 1.69 per cent, with an average of 0.84 per cent. This is sufficient to need consideration when determining the retention of titanium compounds where domestic clay is also present.

The similarity of these clay analyses is evidence that the qualities by which a clay may be judged are largely physical.

Particle size varies greatly in different clays, even in those which appear very similar, and in its complete determination it is necessary to employ sieves, elutriation, and sedimentation. Such methods applied to paper-making clays gave the following data:[3]

PARTICLE RADIUS	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8	No. 9
Above 22μ	0.1	0.1	0.1	0.1	0.1	0.2	0.1	0.1	0.1
22μ–7μ	0.3	9.7	18.3	14.2	12.2	15.2	8.1	15.8	18.5
7μ–1.5μ	10.9	24.1	34.1	41.1	43.2	40.7	39.5	45.2	46.5
1.5μ–0.5μ	40.1	33.1	20.0	21.6	22.8	23.6	32.5	22.2	18.4
Below 0.5μ	48.6	33.0	27.5	23.0	21.7	20.3	19.8	16.5	16.5

The effect of particle size on the rate of settling of undeflocculated clay suspensions containing 19.6 parts of water to 1 of clay and using 200 cc. of clay suspensions of the four clays whose analyses are given above, is shown in Table 56.[15]

TABLE 56

Time interval		Clear Liquid above Clay Suspension			
		Foreign Clay		Domestic Clay	
Hr.	Min.	No. 1	Medium	A	B
		cc.	cc.	cc.	cc.
0	10	13	7	77	14
0	30	53	47	145	40
1	00	109	103	153	76
2	00	126	122	159	132
3	00	136	130	165	142
6	00	152	146	169	153
24	00	162	160	171	164

Gypsum. This is a natural calcium sulfate, $CaSO_4 \cdot 2H_2O$, and is prepared by grinding, calcining, fine grinding, washing, and quick drying to prevent rehydration. The natural product loses about 21 per cent of its weight on ignition, while the calcined filler loses only about 0.5 to 2.0 per cent. It is claimed that an improvement in the dispersibility

of ground gypsum may be obtained by adding a small proportion of a soluble aluminum compound and an alkaline compound such as hydrated lime or calcium carbonate. Since gypsum is soluble to the extent of 1 part in 400–500 of water its retention is low unless the white water system is well closed.

The use of gypsum results in a rather soft paper of good opacity. It tends to fill up the felts, owing to crystallization of $CaSO_4 \cdot 2H_2O$. It has not been found to interfere with rosin sizing and in some cases has even proved beneficial.

Pearl Hardening. This is an artificially prepared, hydrated calcium sulfate, which is finely crystalline in form and has a specific gravity of 2.39. It is usually added in the dry state, and is used in the finer qualities of writings, where a high white color is wanted. Since the crystals are more translucent than fibers, an increase in the amount of pearl hardening reduces the opacity of the paper. Calcium sulfate preparations, either hydrated or anhydrous, are sold under many trade names, as Pearl White, Crown Filler, Pearl Finish, Annaline, Alabastine, and Tissue Filler.

Talc, Asbestine, Agalite. These are all natural magnesium silicates of differing physical properties. As a part of the magnesium in talc is usually replaced by aluminum, it may be regarded as a double silicate with the magnesium largely in excess. Talc is very soft, has a characteristic soapy feel, and is usually of a creamy or greenish white shade. Its specific gravity is 2.6 to 2.9. It is very resistant to acids, solutions of alkalies, and heat, losing no water below a red heat.

Asbestine, or agalite, is a fibrous talc which occurs as an alteration product of tremolite and is extensively prepared in St. Lawrence County, New York. It contains about 87 to 95 per cent of magnesium silicate, with smaller amounts of iron, aluminum, and calcium, and is of a very brilliant white shade. Grades with a high calcium carbonate content are injurious to the rosin sizing of the paper, but the purer grades are not harmful.

Owing to their fibrous nature these materials are well retained in the paper. Talc improves the surface of the paper and its feel, but does not improve its printing qualities as much as clay. It is used in smaller quantities than clay (usually not over 10 per cent); in large quantities it tends to make the paper feel very greasy. With book papers where fine printing is to be done talc must be of high quality to insure that coarse particles do not cause considerable wear on the plates and blur the fine lines. Agalite has practically the same advantages and disadvantages as talc. It causes more wear on machine wires than clay and should not be used in large amounts in papers that

are to be cut or punched, as it dulls the cutting edges rapidly. It also tends to make the paper blacken on calendering more than clay.

Talc seems to be an exception to the rule that fillers seriously reduce the strength of the paper. Lodge[11] found Canadian talc to give a stronger sheet than clay. Others have found talc-filled paper with 32 per cent of talc to have higher bursting and tearing strengths than those with 19.5 to 22.5 per cent of clay.

Barium Sulfate, Heavy Spar, Witherite. These are sometimes used as fillers. Heavy spar is a naturally occurring barium sulfate, and witherite is barium carbonate. The high specific gravity of these materials — 4.2 to 4.5 — causes the retention to be low and makes the paper very two-sided, the wire side being particularly destructive to pens and type. For barium sulfate to be used satisfactorily it should be precipitated in the beater by adding barium chloride followed by an excess of sodium sulfate. Barium sulfate imparts brilliance to a sheet, and hence is used in photographic papers. It is also employed in some special printing papers which have to be very flat.

Precipitated Chalk, Calcium Carbonate. This was formerly used in only a few classes of papers, mostly light-weight sheets such as Bible and cigarette papers. For this it was found best to precipitate the carbonate in the beater by adding calcium chloride followed by sodium carbonate.

Calcium carbonate has always been available as precipitated chalk and waste lime sludge from the preparation of caustic soda, and in the latter form has been a very cheap product. Its general use as a filler was prevented by its interference with the rosin-sizing procedure and by the fact that lime sludge was not entirely satisfactory in respect to color and particle size. In recent years much study has been given to both these problems, and by means of various special sizing emulsions, many of which contain paraffin, it has been found possible to size the paper slightly, though not nearly so well as when clay is used. Methods of adding filler and size to reduce the time of contact have also helped to make its use possible.

Improvements in methods of production have raised the quality of the carbonate, both as to color and especially particle size, so that it now has distinct advantages over clay in imparting color, opacity, velvety feel, and bulk to the paper. These advantages are responsible for its more general employment as a filler and coating pigment. Its use in a mill where part of the papers are clay filled and sized on the acid side, and part are alkaline from the carbonate, brings up a whole series of problems relating to coloring, sheet formation, re-use of white water, etc., and some of these are not easily solved.
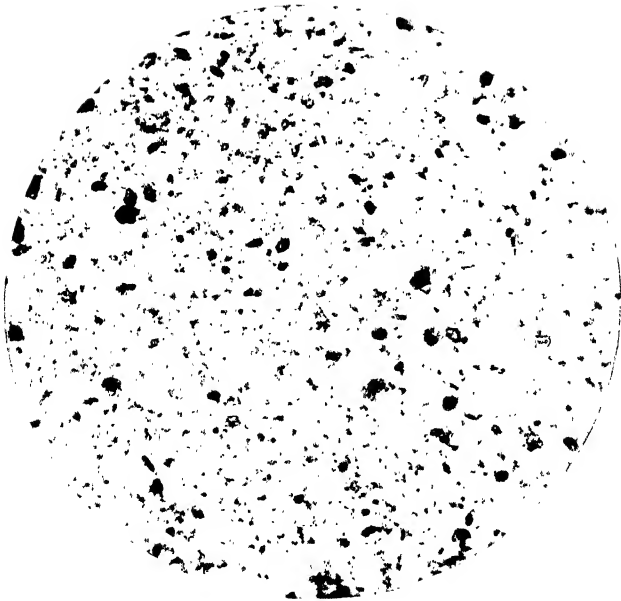
Domestic Filler Clay. Magnification 100 diameters. Photographed by
Bureau of Standards.
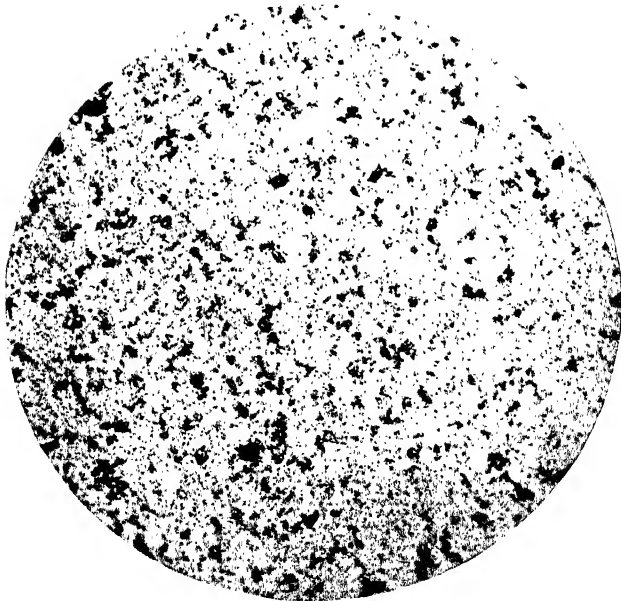
English Coating Clay. Magnification 100 diameters. Photographed by
Bureau of Standards.

PLATE 14

Crown Filler. Magnification 100 diameters. Photographed by
Bureau of Standards.
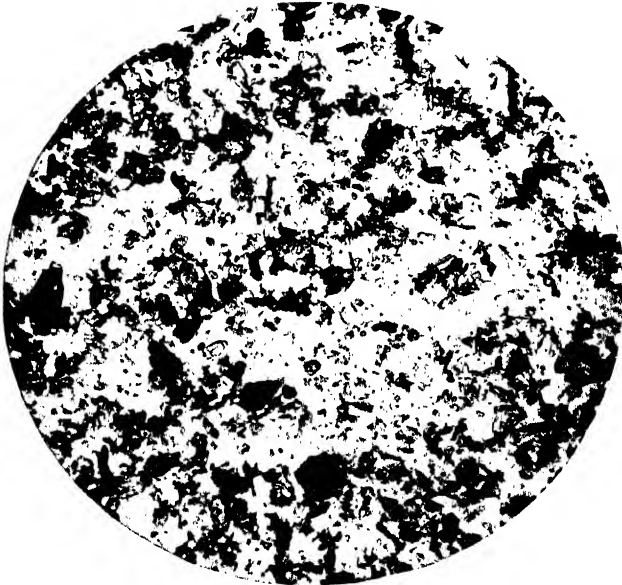
Talc. Magnification 100 diameters. Photographed by
Bureau of Standards.
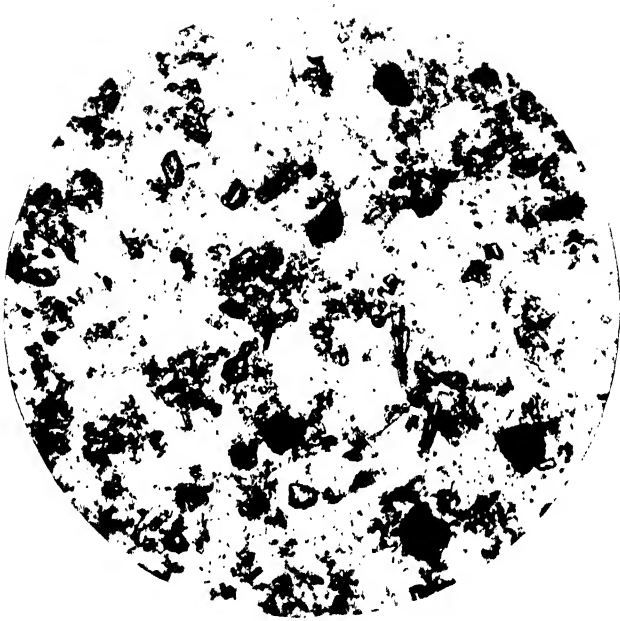
PLATE 15

Asbestine. Magnification 100 diameters. Photographed by
Bureau of Standards.

PLATE 16
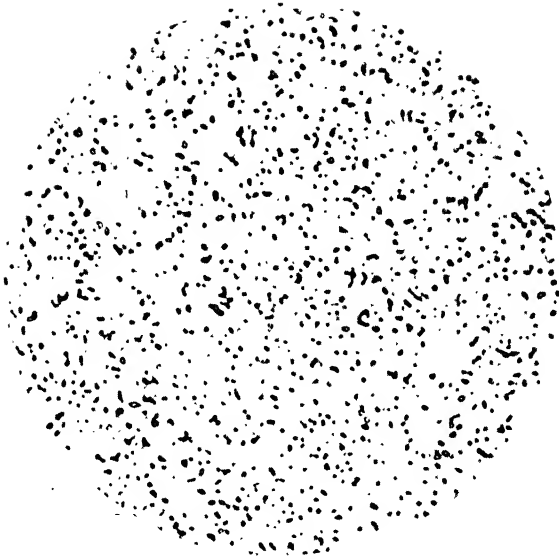
Titanox A.   Magnification 1200 diameters.

Domestic Coating Clay.   Magnification 1200 diameters.

PLATE 17

The methods of preparing these fine-grained products are numerous and many are patented. Some involve causticizing at low temperature and with a high degree of agitation, while others carbonate milk of lime with flue gas under special conditions. According to the variations in the processes the products range down to the colloidal in particle size. When made in such special ways the advantage of cheapness, possessed by waste lime sludge, is largely lost.

Titanium Pigments. Titanium pigments were first produced in 1918, and as early as 1928 the German literature referred to their use in the paper industry. Since then improved quality and lower price have resulted in greatly increased use.

The raw material is ilmenite, which is theoretically an iron titanate, $FeTiO_3$, containing from 35 to 55 per cent of TiO_2.[19] Commercial deposits are found in India, Africa, Brazil, Norway, Canada, and the United States. The ore is first concentrated, then ground to a fine powder and treated with concentrated sulfuric acid. The iron and titanium dissolve as sulfates and are removed from insoluble impurities by settling and washing, after which the solution is adjusted to a definite strength.

For compound pigments the proper amount of barium sulfate, previously made in a separate operation, is added, and the titanium is precipitated by hydrolysis at the boiling point. After precipitation is complete the mass is washed, partly dried, calcined, disintegrated, and air-floated to a fineness of 99.9 per cent through a 325-mesh screen. The average particle size is about 0.5 micron. Compound pigments with calcium sulfate are made in the same way, as are also the pure TiO_2 pigments, which have an average particle size of about 0.2 micron.

The advantages of titanium pigments include high refractive index and small particle size, both of which aid in obtaining high opacity in the paper. This reduces show-through of printing ink and makes the pigments especially valuable for papers which are to be oiled or waxed, since the loss in opacity is much less than in unpigmented sheets. Their high light reflectance — 95 per cent or more as compared with 98 per cent for the standard magnesium block — shows that they will impart whiteness and brightness to the paper, and that small amounts will produce definite color improvement. Their fineness results in excellent printing surfaces, but it is essential that the pigment be thoroughly dispersed, since aggregates, if present, will cause trouble or limit the advantages which should be gained from the pigment.

Another advantage is their chemical inertness; it is claimed that there is no tendency to react with any of the raw materials used in paper-making or finishing operations. Their relatively high cost

calls for care in the design and operation of white water systems, so that good retention may be obtained. Some mills claim as high as 80 per cent, but 60 per cent is probably more nearly a correct average.

Zinc Pigments. The development of zinc pigments as paper fillers has taken place within the last few years and largely as a result of the success of the titanium pigments.

Zinc sulfide has a refractive index of 2.37 and a high degree of whiteness, brightness, fineness, and uniformity of particle size, thus possessing many desirable properties as a paper filler. It is claimed that zinc sulfide absorbs ultraviolet rays sufficiently to afford a certain protection against light, and it also seems to protect papers to some extent from the deteriorating influences of the accelerated aging test. Stable compounds may also be formed with certain printing colors, thus assuring durability of the print.

Zinc oxide has a high refractive index and excellent whiteness, but owing to its reaction with alum it is not considered suitable as a filler. Its antiseptic value is well known, and a similar sterilizing action is claimed for zinc sulfide, with resulting decrease in slime formation and a further possible closing of the white water system.

Lithopones are compound pigments of $BaSO_4$ and ZnS, formed by mixing solutions of zinc sulfate and barium sulfide. The precipitate obtained is washed, dried, calcined, and while still red hot quenched in cold water, which greatly improves its quality. The pigment is then wet-ground, dried, and dry-ground to give a product with a particle size of about 0.25 micron. Lithopone is brilliant white, extremely fine in texture, and has excellent hiding power with a refractive index of 2.0. It normally contains 29.5 per cent of ZnS and 70.5 per cent of $BaSO_4$, but in some cases these proportions are varied, and occasionally some titanium dioxide is added.

The use of these pigments in copper equipment under conditions which permit any copper to dissolve is likely to result in an appreciable dulling of the color. The pH of the stock should not go below 4.5 and preferably should be kept at 5.0 or above.

Testing Fillers. *Moisture* is usually determined by drying at 100–110° C., unless the material is of a nature to lose chemically combined water at that temperature, in which case a lower temperature in a vacuum oven or for a longer time must be used. Chemically combined water is generally determined by ignition at a red heat as in ash determinations.

Color. The color of a filler is chiefly of interest in relation to the effect it will have on the color of the paper, and since this depends on

the refractive index and opacity of the filler particles, as well as on its color, the best comparison is obtained by actually using it as a filler and comparing the color and brightness of the sheets produced. This is too long and complicated for routine tests but is the only safe way when comparing fillers of greatly differing characters.

For comparing two shipments of the same material, or two fillers of the same type, the dry, powdered materials may be pressed down side by side on a black paper and the two surfaces compared. This will show comparatively small differences in brightness, hue, etc.

Some prefer to compare colors in the wet condition, by mixing each sample to a putty like paste, placing approximately equal amounts close together on a clean glass plate, and pressing a second plate down on top. This brings the samples in immediate contact and differences may be easily observed.

These methods are not so satisfactory for the newer fillers of high brightness, for which it is best to use a spectrophotometer or one of the color-measuring instruments employing light filters.

All these direct comparisons of color fail to tell how important the color differences are, and until permissible limits have been set by practical trials, the acceptance or condemnation of a shipment will be on an unsatisfactory basis.

Whether a filler has been artificially blued is not easy to determine. The two methods commonly applied[18] are to note any color change when the material is mixed with lime water, or to mix the filler with water, add a little concentrated ammonia, and evaporate to dryness, when the presence of soluble blue will be shown by a blue stain on the surface of the mass.

Particle Size. Interest in particle size is comparatively recent in paper making. It was formerly believed that clay and many of the other fillers were merely inert materials, but it is becoming more evident that they exert a considerable influence on many of the operations, and some of the answers are being sought in a study of particle size.

The microscope can be used for such determinations, but much time and experience are needed and large numbers of particles must be counted. Moreover the ordinary microscope is limited in range to particles above 0.5 micron in size, and the particles below this are of great importance. Below the range of the ordinary microscope the ultramicroscope can be used to show the number of particles, but not their size, but by combining an ultramicroscope with a hemocytometer and a known volume of colloidal solution it is possible to determine the particle size of a colloid.

Other methods of determining particle size are by sieves, elutriation, and sedimentation, each of which is useful over a well-defined range as follows:[4]

Sieves .... particles over 22 microns radius
Elutriation .... particles between 15 and 5 microns radius
Sedimentation .... particles below 5 microns radius

A complete particle-size analysis, therefore, involves the use of all three methods.

Sieve analysis takes out the coarse material which has often been spoken of as " grit," although it will include any material large enough to be retained by the wire mesh used. Unfortunately there are three distinct sieve specifications: (1) National Bureau of Standards; (2) Institute of Mining and Metallurgy; and (3) the British Standard; therefore, in recording results it is important to state what sieve specification was used. The National Bureau of Standards sieve sizes are shown in Table 57.

TABLE 57

Sieve No.	Maximum Particle Radius Passing Sieve
	Microns
325	22
270	27
230	31
200	37
170	44
140	53
120	63
100	75

In making sieve tests it is usual to place 100 grams of the filler in a bottle with 1 liter of water, allow it to soak a short time, shake vigorously, and pour onto the sieve. The clay is washed through the screen with a stream of water, using a camel's-hair brush to flatten out any lumps, and the residue is dried and weighed.

The fundamental principle of elutriation is that an upward current of water will carry away all particles below a certain limiting size, which depends on the velocity of the current. The relation of these two factors for water at 20° C. is shown in Table 58.

For satisfactory elutriation a stable deflocculation of the pigment is essential, and the temperature of the water is of great importance.

Elutriation is not a simple process but demands great care and a thoroughly studied technique; unless proper precautions are taken serious errors may result.

TABLE 58

Limiting Particle Radius	Velocity of Upward Current of Water at 20° C.
Microns	Mm. per sec.
15	0.81
12	0.53
10	0.36
8	0.23
7	0 18
6	0.13
5	0.089

The sedimentation process for determining fractions below 5 microns consists essentially in suspending the deflocculated filler in a quiescent condition and noting the rate at which particles settle to the bottom, from which their radii may be calculated by means of Stoke's law. Complete deflocculation and temperature control are fully as important as in elutriation. The periods of quiet sedimentation corresponding to various particle sizes are shown in Table 59.

TABLE 59

Particle Radius	Settling Time, t
10 μ	4 min. 38 sec.
5 μ	18 min. 40 sec.
4 μ	29 min. 0 sec.
3 μ	51 min. 30 sec.
2 μ	1 hour 56 min.
1.5 μ	3 hours 26 min.
1 μ	7 hours 43 min.
500 mμ	31 hours 7 min.
200 mμ	193 hours

t = time taken by particle to fall through a height of 10 cm. in water at 20° C.

Much study has been given to sedimentation processes, and fairly accurate results can be obtained with comparatively simple apparatus. Among the more important methods are the following:

The Odén-Keen automatic recording balance[2] gives a continuous record of the mass settling on a balance pan suspended in the medium.

The pipette method[10] removes portions of the suspension at a given depth at various times.

Wiegner[26, 12, 23] measures the progressive decrease in hydrostatic pressure at a point in the suspension by means of a manometer attached to the sedimentation vessel.

Bouyoucos[1] uses a specially designed hydrometer, graduated in grams of clay per liter, to show the progressive fall in concentration with time of settling.

In the turbidity method[23] a beam of light passes through an optical cell containing the clay suspension and falls on a photoelectric cell.

In the beaker method[14, 6] the clay suspension is separated into fractions by decantation after different periods of time.

All these tests are too long and intricate for control tests, or for use in the average paper mill laboratory, but they serve well in research problems.

Methods of Applying Fillers. *Beater.* Since the earliest use of fillers it has been general practice to add them dry to the stock in the beater. This provided an easy means for using measured quantities and for mixing with the fibers, but all the dirt and foreign matter in the filler went directly into the paper stock. To avoid this it is now customary to make the filler into a slurry with water, screen this through a vibrating or oscillating type of screen, and add a definite amount of the screened slurry to each beater. Slurries of 20 per cent consistency can be handled readily and with many clays this may be increased to 50–60 per cent if some dispersing agent, such as silicate or phosphate of soda, is used.

The usual sequence in beater furnishing is to add the filler as early as possible after the fibers, and follow with size, alum, and other materials. This insures thorough mixing of the filler with the fiber and gives the maximum time for breaking down any lumps which it may have contained. This is usually unimportant with slurries of china clay and similar fillers, but the titanium pigments are likely to contain small aggregates of particles which are hard to disperse and which reduce the value of the filler if they are not fully broken down. This difficulty has been overcome to a considerable extent by the development of types of the pigments which break up more easily and by the use of dispersing agents to aid in " wetting " and suspending the pigment.

The addition of the filler to the beater is advocated by those who believe that its close contact with the fibers and " fibrils " allows it to be " beaten into " the fibers, thus improving its retention and the opacity of the paper. This is difficult to prove, as it has been shown that an almost identical effect can be obtained by adding the well-

dispersed filler after the completion of the beating and jordaning processes.

Some fillers which have desirable properties are too soluble to add at the beater, and others, such as calcium carbonate, are too unstable under the usual beater conditions when an excess of alum is present. If the pH of the stock is not brought below 7 the rosin sizing is unsatisfactory, while if sufficient alum is present to accomplish this, much of the carbonate is destroyed and serious foaming occurs.

The answer to this trouble seems to be delayed addition of one of the reacting chemicals so as to minimize the time of contact and limit the reaction as much as possible. Thus, if the calcium carbonate is added to the stock just before it reaches the paper machine, very little reaction takes place; foaming is not serious; the filler retention is increased; and fairly good sizing is obtained.

Fillers are used to some extent for the prevention of pitch troubles on the paper machine; among the effective materials are china clay, bentonite, witherite, and diatomaceous earth. It is probable that these substances have the property of absorbing the small pitch particles and preventing them from agglomerating to start the accumulation of relatively large balls or lumps of pitch, which eventually cause trouble by adhering to the suction boxes, Fourdrinier wires, and press rolls. Usually 1 or 2 per cent of a material such as " cellite " (a diatomaceous earth) will considerably reduce the tendency to accumulate pitch on the paper machine.

Addition on the Paper Machine. Studies of retention had shown the importance of a proper white water system and of the filtering action which occurs on the paper machine during sheet formation. Great losses of both filler and fine fiber take place during the early stages of sheet formation, but as this progresses, the web acts more and more effectively as a filter, and by the time the sheet reaches the suction boxes the loss in the white water is very small.

It was realized that if the filler were not added before the stock reached the paper machine, but could be added after the web was partially formed, the initial loss could be eliminated and later losses through the web would be small. The difficulty in developing the method proved to be in producing a uniform film of filler slurry and delivering this at an even rate to the forming web on the paper machine. Many methods were tried, and the most practical was found to be the use of spray nozzles with a delivery baffle.[5]

Machine filling is not applicable to all grades of paper, and whether it will prove advantageous depends on several factors, such as the type of white water system used, the weight of paper made, the

degree of beating (hydration) of the stock, and the formation of the sheet.

If the white water system is completely closed, there should be little gain in retention by filling on the machine. Few systems are completely closed, because of the tendency to slime formation, which is greater as the filler content in the water increases. Machine filling reduces the filler consistency of the white water and tends to minimize slime.[8]

Machine filling is usually advantageous for all weights of paper, but the point of application must be adjusted to the weight made. For light papers the filler should be added near the suction boxes so as to utilize the fiber mat to the fullest extent. With heavy, thick paper little filler can pass through the forming mat and the addition must be made as close to the stock inlet as possible, thus permitting some mixture of the filler with the stock, so that part of it may be drawn into and through the forming web. Papers ranging from 15 to 50 pounds per ream, $24 \times 36 = 480$ sheets, are being filled by this method.

Increased hydration of the stock greatly increases the effectiveness of machine filling, and close formation gives a more dense mat of fibers and a more effective filtering medium.

Retention. Retention may be defined as the percentage of the filler added to the furnish which appears in the finished paper. It is greatly influenced by many manufacturing conditions, and may range from 30 to 90 per cent, with an average of about 60 per cent. Investigations of the factors influencing retention have led to extensive studies of the fillers themselves and to a much fuller understanding and more rational use of white water.

The mechanism of retention is still not fully understood, and its dependence on many variable factors which must be studied on a manufacturing scale makes experimentation very difficult. Haslam and Steele[7] consider that there are three ways in which fillers may be retained in paper: (1) filtration, (2) coflocculation, and (3) mechanical attachment; Willets[27] mentions simple filtration and colloidal attraction. Of these terms, " filtration " means the retention of the filler in the web because the spaces between the fibers are smaller than the pigment particles themselves. " Coflocculation " assumes the attachment of the pigment particles to the fiber walls through the play of interfacial forces analogous to those causing flocculation. " Mechanical attachment " relates to that portion of the pigment which cannot be removed by repeated washings and which is held on the fibers by forces much greater than those of coflocculation.

The factors affecting retention may be considered as relating to the

fibers and their preparation, to the paper-machine operation, to the fillers themselves; and to miscellaneous influences.

A long fiber capable of good fibrillation is considered most favorable for high retention, and its capacity to impart increasing density to the sheet seems responsible for its superiority. Some of the common fibers rated in the order of retention capacity are: cotton, sulfate, sulfite, straw, and groundwood. This order might be materially altered by changes in the relative degree to which the fibers were beaten, for an increased "hydration" or "wetness" of the fiber results in an increased retention, probably due to the increase in the surface of the fibers, with better felting and a consequent better filtering action. Filler is retained in paper made from unsized, unbeaten pulp purely by filtration; the filler does not aid in forming a filter mat.

Increase in sheet weight causes increased retention, as would be expected, because the thicker fiber mat offers greater resistance to the passage of filler particles; this effect is more pronounced in the lighter weights. The greater the dilution of the stock passing onto the wire and the greater the speed of the machine the lower the retention because of the more rapid removal of the water. Increase in suction, whether by boxes, couch, or press, tends to reduce retention by removal of filler, especially from the under side of the sheet. On the other hand, the finer the mesh of the machine wire the better the retention, due to the more compact bottom layer upon which the remaining part of the web is built. Temperature of stock also affects retention; work on titanium dioxide has shown an increase with increasing temperature.

The more highly the colloidal properties of the filler are developed the greater is its tendency to adhere to the fibers. Since it is possible to obtain good retention with fillers of relatively coarse as well as extremely fine particle size, it seems that the other factors have more influence on retention than the properties of the fillers themselves. It also appears that the specific gravity of the filler has no appreciable influence on retention. The amount of filler used has an important bearing on its retention. It is well known that large amounts are difficult to retain, even in heavy sheets, and that very small amounts are poorly held because of its great dilution in the stock going to the machine. It is probable that the amount of filler retained increases with increase in concentration up to a maximum and then is constant.

Rosin size and alum aid clay retention, and higher retentions are found with hard-sized sheets; alum without size increases retention only slightly. With talc the retention is less in the presence of size and alum than with alum alone. The acidity of the stock (pH value) is generally thought to have a very definite effect on retention, but acid is not a

substitute for alum in water purification or paper sizing, and it is possible that the precipitated alumina, and the flocculating condition induced, are the important conditions, and the acidity merely incidental. Whatever the reason, insufficient alum causes poor retention.

It is not clear whether starch in the beater always improves the retention of filler; it is possible that under certain conditions it may be helpful and under others detrimental. It has been suggested that the protective colloidal action may prevent loss of filler, and also that this action may maintain the filler in such a well-dispersed state that it could not be coagulated and fixed on the fibers. Willets,[28] working with titanium dioxide, found that starches differed in their action, but that none aided retention.

Retention is increased by the use of very small amounts of flocculating agents mixed with the stock containing alum, as it passes to the wire of the paper machine. The Sveen process[17] mentions solutions of animal glue, such as joiners' glue, fish glue, and that made from leather waste, as well as casein, various soap solutions, and rubber milk. With hide glue it is preferred to age the solution at room temperature, or lower, and to avoid violent agitation or long standing after it has been added to the stock. The amount necessary is only 1 to 3 pounds per ton of paper.

Wetting agents to reduce surface tension and the interfacial tension between solid and liquid have been found necessary in making certain pigments, mainly to reduce grinding time. Their application in paper filling has not received much attention but would seem to offer interesting possibilities. The present procedure appears to be the use of sodium silicate, ammonia, phosphates, etc., in order to disperse the filler more completely before it is added to the fibers.

The method or order of addition of filler and other materials is of considerable importance. The point of addition of alum may raise the retention as much as 25 per cent, and better results seem to be obtained the nearer the head box it is added. Since a large loss of filler occurs during the first few feet of its passage over the wire it is necessary to close the white water system in order to obtain good retention. If completely closed, and if it becomes overloaded with filler, it is hard to avoid the formation of slugs and slime. Even with a well-closed system the filler retained during the first of a run is generally low and builds up as the run progresses. This points to the need for a means of leveling out the ash in the sheet and providing for ready adjustment of its amount.

A determination of retention, if carried out in the most accurate way, must take into account the weights of all materials — fibers, size,

alum, fillers, etc. — added to the beaters and also their ash content, or in the case of the fillers, their loss on ignition. From these data and a determination of the ash in a representative sample of the stock it is possible to calculate how much of the ash at this point actually comes from the filler as such.

At the other end of the machine careful records must be kept of the weights of paper made and its ash content, and from this, by applying corrections for ash in fibers, etc., it is possible to calculate the weight of filler appearing in the paper. This weight, divided by that added to the beater, gives a figure for percentage retention which is usually accepted but not entirely free from errors. It is obvious that it does not take into account the amount of wet or dry broke made in running the stock into paper and so does not credit as retention filler which was actually carried over the wire but not weighed as acceptable paper. Another error is that the filler as determined by ignition of the paper or stock is not calculated on the same basis because the ratio of filler to fiber is not the same.

Because of the very large amount of work necessary to get an approximately accurate figure in this way, it is suggested that retention be calculated by the following formula:

$$\text{Retention} = \frac{0.94B(100 - C - A)}{A(100 - C - B)}$$

in which A = percentage of ash in air-dry stock going to the paper machine.

B = percentage of ash in air-dry paper made.

C = percentage of bone-dry filler lost on ignition.

All these percentages are considered whole numbers, and the formula assumes a loss of 6 per cent of fibrous material in passing over the wire.

This formula will show different figures for retention according to where the sample of wet stock is taken. If this comes from the beater the retention will be based on the filler added plus that furnished with the broke or old paper stock; if it is taken at the head box of the machine it will show what proportion of the total filler going onto the wire is appearing in the finished paper. It has the advantages that it is not necessary to weigh all the paper made, but only to determine the ash in representative samples; and also that it calculates the ash on the basis of the fiber present rather than the entire stock or paper, and thus makes the ash figures directly comparable.

The above formula may be used to obtain a figure for retention at any stage in the production of beater filled stock, and does not involve the

necessity of waiting until the run has been completed to obtain a retention figure. It is not suitable for the calculation of retention by special filling methods, however.

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CHAPTER XII

COLORING

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The importance of color to the paper industry is not always evident to the casual observer; actually, very few papers are made without coloring matter of some kind. This is self-evident in heavily colored papers, or even pronounced shades, but it is equally true of white papers, for very few are the natural color of the fibers. In a way, coloring as applied to the production of shades of white is of more importance than in making of colored specialties, for the production of the former runs into far greater tonnage. The maintenance of uniformity in a tinted white requires more care than with deeper-colored papers, for a slight error in the amount of color used will make an appreciable difference in the resulting shade, whereas with deeper colors an error of the same magnitude will have hardly noticeable results. Variations in the color of the fibers used are also much more serious in the case of tints than they are with deeper colors.

In coloring paper it is usually required that a submitted sample be matched, and at the same time specifications for fastness to various use conditions must be met. To accomplish this it is seldom necessary to identify fully the coloring matter in the sample, as tests for fastness to light, acid, alkali, and bleach will usually show the nature of the predominant dye in a heavily colored paper. The color of the ash remaining after igniting the paper will sometimes indicate the nature of the pigment used. In white or lightly tinted papers these tests are less reliable because changes in the fastness tests of the colors are masked by those in the fibers themselves.

If full identification of the dyes must be made, which is a complicated and laborious task, reference should be made to Grant,[2] who discusses the identification of coloring materials by chemical and fluorescence tests from the standpoint of dating papers; to Herzog,[6] who describes microscopical methods for identifying white and colored pigments; and to the systematic schemes for color identification of Green[3] and Mulliken.[8]

Coloring paper is an extremely complicated job and few appreciate what the color man must contend with. He must not only know

coloring matters, but must also consider the kind of fibers used and the amount of beating given, the condition of the water, the presence of rosin size, alum, and the various fillers, the speed of the paper machine, and the suction applied. Coating brings in an entirely different set of conditions involving the relation of the coloring matters to glue, starch, and casein, different white pigments, different drying conditions, and different surfaces. The handling of dyes and colors is one of the more important jobs in the mill, and those entrusted with this duty should have a keen sense of color perception.

The colors used in paper may be divided into two general groups, pigments, which are insoluble materials, and dyes, which are employed in solution. Each of these groups may be subdivided into others according to certain characteristics.

Pigments. These include all colors which are not strictly soluble in water and which are held in the paper by mechanical means. They may be divided into groups, as earth pigments, colored metallic salts, carbon blacks, vat colors of the anthraquinone series, and lakes prepared from dyes.

Pigments are usually very fast to light but dull in shade. Their reactions toward acids and alkalies vary with the individual substances; the majority are not bleached by hypochlorite and must be avoided if bleachable waste stock is desired. They add weight to the sheet, but if used in considerable quantities they tend to weaken it as do other fillers.

Pigments should be added to the beater as early in the cycle as possible in order to insure good dispersion. Their retention is increased by alum and by increased hydration of the fibers as beating proceeds; this often makes it difficult to control the results obtained. The back-waters from heavily pigmented papers are always colored, but the colors in the paper bleed only very slightly when in contact with water.

Though the pigments, especially the earth colors, are gradually being replaced by dyes they are still used for special purposes and a number of them are of considerable interest to the paper maker.

Ochres depend for their coloring power upon ferric oxide or hydrated ferric oxide, and various shades from yellow to brown are obtainable. The best are fine powders, soft to the touch, and possessing plastic properties; dark-colored brands of this nature are generally richest in coloring matter. Ochres are sometimes mixed, or " topped," with chrome yellow to produce more brilliant shades; such products possess the defects of chrome yellow and if used without proper precautions may cause trouble.

The red earths owe their coloring power to the presence of amorphous ferric oxide, the chief ingredient in red hematite, which is the basis for numerous colors. Other reds are obtained by heating clays containing hydrated ferric oxide to a red heat. This class of colors includes a number of " red oxides," varying from yellowish to bluish red, and also Pompeian and Venetian reds which are usually less strong than the " oxides."

Among the brown earth colors are " velvet," " umber," and " chestnut " brown, which depend upon burnt ferric hydrate for their coloring power. True umber consists mostly of manganese silicate, which is greenish brown in its natural state but becomes a rich, deep brown on burning.

These natural mineral colors are largely used in the production of wallpaper, for which their subdued shades, fastness to light, and resistance to atmospheric influences render them especially suitable.

Artificial mineral colors are still used quite extensively in the coloring of certain classes of paper; among those which are still relatively important are chrome yellow, Prussian blue, and ultramarine.

Chrome yellow may be obtained either as a dry powder or in the paste form. It is somewhat sensitive to alkalies and also to heat, so careful handling on the dryers is necessary if irregular results are to be avoided. Chrome yellow is very fast to light but is destroyed by hydrochloric acid. Caustic soda or lime milk converts it into chrome orange, or basic lead chromate, but this color can be used for unsized papers only, as it reverts to the yellow form in the presence of alum. As the lead salts are dangerous poisons they should be avoided whenever other coloring matters can be substituted.

Prussian blue is classed as a mineral color because of its iron content. It is affected by alkalies, particularly caustic soda, which destroys the color with the formation of ferric hydrate; treatment with acid restores the color. When using it in the beater it is well to see that it is added while the reaction is slightly acid from the presence of alum. Paper colored with Prussian blue is partially decolorized by sunlight, but the full blue shade is developed again when the paper is kept in the dark in contact with air.

Soluble Prussian blue is produced when a ferric salt is added to an excess of a solution of ferrocyanide, or if Prussian blue is boiled in a ferrocyanide solution. It is soluble in water but is precipitated by salts.

Ultramarines are manufactured in various shades of blue from a greenish to a reddish tone, and there are even pure greens, which, however, find little use in coloring paper because of their tinctorial weak-

ness. They are made by heating mixtures of clay, sodium sulfate, sodium carbonate, sulfur, silica, and charcoal; the mixture after heating is finely ground and washed. The proportions of the ingredients vary with the different manufacturers, but in general three grades are made as follows:

1. Sulfate ultramarines are those made with sodium sulfate. They are the palest, are greenish in tint, and are most easily attacked by alum.

2. Soda ultramarines low in sulfur are pure blue and darker than the sulfate ultramarines.

3. Soda ultramarines high in sulfur and silica are the darkest and have a reddish tinge. They are the most resistant to alum.

The finished ultramarine contains sodium, aluminum, silicon, sulfur, and oxygen; its actual constitution is not known, and no theory so far proposed accounts for all its properties. Ultramarines are absolutely fast to light and are not changed by exposure to the atmosphere or by weak alkalies. They are decomposed by mineral acids with evolution of hydrogen sulfide and destruction of the color. Even the most acid resistant are so affected by alum that there is considerable loss of color in stock which has to stand over the week end; it is always found necessary to touch this up with a little more color before starting up after a shutdown.

Ultramarines are darkened by moisture, and sometimes water, glycerine, or molasses is added to make them appear of greater strength. For this reason they should not be purchased on the basis of their appearance but actual coloring tests should be made. The different products vary in particle size and the ease with which they disperse in water, and if an ultramarine does not satisfy both requirements spots or color streaks are likely to appear in the paper.

When used for tinting white papers ultramarines give bright effects which are hard to equal with other coloring materials. If they are used for deeper colors the paper is likely to be two-sided because of the loss of pigment in passing over the suction boxes.

Another pigment which is still used occasionally for gray or black papers is lampblack. Its low specific gravity makes it difficult to handle without getting it all over the beater room, and if used in large proportions it tends to cause streaks and specks in the paper. Uniform results are hard to obtain because the shade depends so much on the degree of the beating which the stock has had. If more than about 4 per cent of lampblack is used it crocks or smuts badly; greater depth of shade may be obtained by simultaneous use of a soluble dye.

Organic pigments of the anthraquinone series were introduced under the name of " Indanthrenes," and later similar colors of somewhat im-

proved brilliance were brought out under other trade names. Few of these have found a permanent place in paper coloring because of their cost and the fact that bright shades were not obtained; their chief advantage is fastness to acid, alkali, and bleach.

Lakes are organic dyes which have been precipitated on mineral bases, usually as barium, aluminum, lead, or calcium salts. The bases employed include aluminum hydrate, gloss white $(Al(OH)_3 + BaSO_4)$, blanc fixe $(BaSO_4)$, satin white, basic aluminum sulfate, etc. The reactions involved in preparing lakes appear simple, but the trouble comes in duplicating results. Such factors as the rate of precipitation, temperature, speed of agitation, and type of equipment are important, and unless they are very carefully controlled the product is bound to vary, both in coloring power and softness. Considerable differences in color and tone may even exist with no differences detectable by chemical analysis.

Lakes are usually prepared from the basic colors, which in this form are much faster to light and less likely to bleed in contact with water. Comparatively few of the acid colors are suitable for making lakes, and little can be done to improve their permanence. One of the more recent groups of lake pigments is made by precipitating a basic dye with phosphotungstic acid, and as methyl violet and victoria blue are generally employed the products vary from red to blue in tone. These colors are readily dispersible in water to colloidal suspensions and are precipitated and fixed on the fiber by alum.

Direct Dyes. These dyes may be used on fibers in a neutral or alkaline condition without the aid of mordants, such as rosin size and alum, and in fact alum reduces their brightness and fastness to light. For waterleaf papers, heating to 130° F. or higher and the addition of 40 to 75 pounds of salt to a 1000-pound beater aid in maintaining uniformity of color and in fixing the dye on the fiber so that the back-water is practically colorless. Under these conditions, and with a final washing of the colored stock, it may be used in making granite papers, which require that the color shall not bleed from the fiber.

Direct dyes may be mixed in solution with acid dyes, but never with basic dyes, as they precipitate each other. They are usually sensitive to hard water, being precipitated by lime or magnesia. They are taken up more rapidly by unbleached than by bleached fibers and so tend to give granite effects when used in a mixed furnish. If possible the pulp with the least affinity for the dye should be furnished first, followed by the color and then by the more receptive fiber.

Some of the direct dyes are unbleachable while others bleach readily. They are considerably affected by pH changes, and it is important that

the acidity be maintained at the optimum point, which varies somewhat with the different dyes. The direct dyes may be used for sized papers if the water is made soft by a little soda ash before adding the color; this insures the absorption of the dye by the fiber, after which the alum does very little harm. Congo red and benzopurpurine are injured by alum, but good results can be obtained by adding just enough soda ash to restore the shade before dumping the beater.

As a class the direct colors have less tinctorial power than basic or acid colors, but most of those which are used in paper are faster to light and other deteriorating influences.

Basic Colors. Basic colors are salts of organic bases which contain the color-bearing group. These color bases are precipitated from solution by the addition of an alkali. Most commercial basic colors are hydrochlorides, though sulfates, acetates, oxalates, nitrates, or even double salts of hydrochloric acid and zinc chloride are also met with, and in rare cases the color base is used. All basic colors are decolorized by reducing agents as zinc and hydrochloric acid. Some decompose into other substances so that the color cannot be regenerated, but with most a colorless or "leuco compound" is formed which is easily oxidized to the original color. In dyeing with basic colors the salts decompose, the basic part combining with the acid present in the fiber or fixed thereon by mordanting with tannic acid. The nature of the mordant or of the fixing metal does not greatly affect the shade of any given dye.

Basic colors have very great tinctorial power and are generally of pure and brilliant shades. They are fugitive to light, but because of their great coloring power they are extensively used where permanence is not of the utmost importance. The affinity of all fibers for basic dyes is not the same, so mixtures are likely to dye unevenly; a little alum added before the color and the use of very dilute dye solutions help to avoid this. When the fibers have a considerable affinity for the color, as with sulfite and jute, the dyeing may be done with the aid of rosin and alum or even alum only, but for maximum fastness, as for use in granite papers, mordanting with tannin is necessary. Unbleached sulfite tends to absorb the color strongly, and the use of dilute dye solutions is quite essential. For groundwood pulp basic colors are especially suitable and the dyeing should be done hot.

When either basic or direct colors are used for a mixture of groundwood and unbleached sulfite it is well to furnish the groundwood first, then the color, and, after thorough mixing, the unbleached sulfite. Most of these colors are taken up by unbleached sulfite much more

quickly than by groundwood and the method given reduces mottling to a minimum.

Basic colors may be used mixed with each other but never mixed with either acid or direct colors since precipitation results. If it is necessary to use both classes of color they should be dissolved separately and added separately to the beater. Many of the lakes formed by basic and direct colors are decomposed at 70° C., or even below, so where both are used it is well to avoid high temperatures. The use of acid and basic colors together gives colorless back-water; for the best results it is well to use the basic dye first and top with the acid color.

Basic dyes are sensitive to water containing lime or magnesium salts or free alkali. Under such conditions a little acetic acid in the water will make the dye dissolve more easily. Auramine, Chrysoidine, and Basic Brown are sensitive to heat when in solution and should not be heated over 160° F. when dissolving; other basic colors may be boiled if necessary, but it is better to dissolve them at 160° to 180° F.

Acid Colors. Acid colors are of three groups: (1) nitro compounds, (2) azo compounds, and (3) sulfonated basic colors. Reducing agents decolorize them but affect them differently: nitro compounds are converted into amino compounds from which the coloring matter cannot be regenerated; azo compounds decompose with breaking up of the azo group and cannot readily be linked up again, while the sulfonated basic colors form leuco compounds from which the color can be regenerated.

Acid colors can be mixed with each other to produce compound shades. They are not suitable for unsized papers as they have little affinity for fibers and cannot be fixed on cotton or linen to resist washing. Rosin sizing is essential for good results, especially for deep shades, and fixation is better if the color is added and thoroughly mixed before the size is added.

Acid colors generally have less tinctorial power than basic colors but dye more evenly and are faster to light. They vary considerably in their reaction to acidity, and the stock on the wire must be maintained at the optimum pH range in order to obtain the highest retention. Acid colors topped with basic dyes are sometimes used to obtain colors which are fuller than those with acid dyes alone and faster to light than those from basic dyes.

Papers colored with acid dyes bleed easily in water or alcohol; they vary in their fastness to acids, but all discolor with alkalies, and all are bleachable.

Mordants. The coloring of paper pulp is not only a question of forming and fixing colored precipitates and pigments, but also of fixing

the soluble colors firmly on the fibers by means of mordants. Soluble colors which form no precipitates with metallic salts and are not fixed on the fibers when the pulp is acidified are of no use in coloring paper. Mordants serve to fix the color upon the fiber and make it more fast to washing, light, etc., or they combine with the dye as an essential constituent without which it would be uncolored or a worthless shade. Mordants are of two general classes: acid mordants, such as tannic acid and the fatty acid compounds used for fixing basic dyes; and basic mordants, consisting of the hydrated oxides of the heavy metals as tin, copper, chromium, iron, or aluminum which serve for fixing the acid dyes. Basic mordants are employed in the form of soluble salts, such as the sulfate or acetate of aluminum, which react with the fiber with the deposition of the base, which then attracts and fixes the color. Time is required for this reaction, and different mordants give different colors with the same dye. Cotton has little affinity for ordinary metallic salts, but if they are present in very basic condition it may decompose them with the loose fixation of metallic hydroxides. Tannic acid, on the other hand, has a direct affinity for cotton and may be still more firmly fixed by the use of tartar emetic or glue. Linen is similar to cotton but is even more difficult to dye. While not strictly a mordant, rosin size gives to fibers some of the properties of animal fibers and enables them to take up many colors without any other mordant.

The use of mordants, other than rosin sizing, is not nearly so general in the paper industry as in textile work, and in many mills they are never employed.

Beater Coloring. This involves the consideration of many factors which must be properly balanced in order to produce satisfactory results at reasonable costs. Of first importance is the kind of paper to be made and its use, for such requirements as cost, permanence of color, bleeding, acidity or alkalinity, fiber furnish, and sizing will definitely limit the colors to be employed. Having established what type of color can be used, the method of handling it and factors affecting its application must be considered.

Beating has a marked influence, and for a given amount of color added, either dye or pigment, the more the fibers are beaten the greater the depth of color produced. Uniformity is therefore dependent on holding the beating within reasonable limits, and this is more important for papers from hard-beaten stock than for those where the beating is slight.

The water must be right for the dye used, and if it is not, correction must be made with acid or alkali as the case demands. For the best results the final pH value of the stock going to the wire must be held

within a certain range, but as this varies with different dyes no general rule can be given. The pH at the time of adding the color to the stock is also important; acid colors may be added to a slightly alkaline stock, but with basic colors this might permit so much destruction that the full color would not be developed on addition of alum. The possible presence of iron in the water must be considered as it discolors the fibers and acts as a mordant with the production of bad shades.

Harrison[4] gives the results of an extensive study of dye retention by fibers under various conditions of pH, temperature, time, consistency, freeness, etc.

The presence of filler and its kind and amount are very important factors in coloring. The use of 20 per cent of filler in a beater usually necessitates the use of 30–40 per cent more dye than if no filler were added. Many fillers have the property of absorbing dyes and thus aiding in obtaining even shades, but they tend to increase two-sidedness, because the filler carries color with it from the under side of the sheet. If it is desired that the filler absorb as much color as possible it should be added to the beater after the dye but before the size.

Heuser[7] finds the amount of dye taken up by different fillers to vary considerably with the different colors. When 10 grams of filler were treated with 0.4 gram of color the percentages adsorbed were as shown in Table 60.

TABLE 60

	1	2	3	4	5	6
Color	Asbestine	Blanc Fixe	Bohemian Earth	China Clay	Kaolin	Talc
Malachite green	96.65	32.40	28.62	45.32	72.75	49.95
Crystal violet	99 97	25.96	62.93	56.91	64.68	60.56
Manchester brown	97.83	28.25	40.00	40.87	72.86	40.62
Safranine	84.82	33.10	53.48	66.45	41.12	30.06
Chrysoidine	96.10	25.82	62.35	41.87	55.91	35.52
Alkali blue	66.10	15.52	48.35	31.75	25.73	35.26
Acid magenta	60.81	18.70	40.07	45.29	26.00	49.89
Ponceau	58.42	23.10	31.89	44.15	22.50	54.27
Cotton scarlet	68.75	33.47	41.00	45.62	20.25	60.12
Napthol yellow	25.00	5.75	5.00	16.52	0.52	25.45
Diamine green	58.50	19.61	32.58	37.92	35.45	50.00
Dianil blue	96.32	30.45	48.03	38.09	53.93	60.76
Diamine violet	68.48	31.84	29.53	35.57	52.95	69.11
Diamine heliotrope	60.59	31.17	46.25	39.71	30.24	65.85
Diamine purpurine	59.89	50.02	47.51	56.14	43.93	60.48

Acid colors can be washed out of fillers almost completely with hot or cold water; basic colors fix themselves more firmly on silicates but can be washed out of blanc fixe.

In filled papers a proper balance of the pigments and dyes will lessen two-sidedness by assuring that the filler and fibers are colored so nearly the same that the difference in the pigment-fiber ratio on the two sides is made less obvious. A dye with little affinity for filler will give a paper which is darker on the wire side, and basic colors which have a strong affinity for clay are sometimes necessary to counterbalance this tendency.

Two-sidedness in unfilled papers is due largely to the arrangement of the fibers themselves. The light reflection from the more or less parallel fibers on the wire side is quite different from that from the fibers arranged heterogeneously on the felt side, and an apparent difference in color results.

A brief comparison of calcium carbonate and clay as fillers showed that they affected the fastness to light of basic colors about equally; acid colors were injured by the carbonate, but direct and pigment colors were not seriously altered. The phosphotungstate blues were not affected, except those toned by Prussian blue, where the latter was destroyed and the color unsatisfactory with carbonates.

The addition of coloring matter to the beater must be governed by conditions. Pigments are best added as early as possible and may be used dry, in the paste form or, better still, after thorough grinding in a pebble mill. Dyes should be dissolved in soft water and strained through a fine sieve before use. Some dyes of unusually good solubility are often added to the stock in the dry state, but it is not good practice.

The strength of the solution is of importance in mixed furnishes, and to avoid " granite effect " the solution should be as weak as possible. It has also been recommended that a few pounds of clay be mixed with the color solution before use.

Coloring Coatings. The coloring of coating mixtures for application to paper surfaces has never had so much study and publicity as beater coloring, yet very important problems are involved.

For toning white papers or making light shades soluble colors may be used provided they are sufficiently fast to the alkaline conditions which usually prevail in coatings. Some of the direct, basic, and acid colors are suitable for coatings, but each color must be studied as an individual until experience has shown whether it is safe for the papers in question.

For heavy colors the use of soluble dyes is generally impossible because their low solubility limits the amount which can be dissolved in the small quantity of water present in coating mixtures. They are also likely to cause differences in color if drying conditions vary, as in the top and bottom of a drying loop, and a very important count against them is their propensity to bleed, due to their lack of affinity for the constituents of the coating mixtures.

These considerations, as well as that of fastness to light, point to the use of pigments in coatings where the color is at all deep, and even for toning whites the only really satisfactory blue is a pigment — ultramarine. For this purpose the phosphotungstate blues have not proved satisfactory and they are probably never used for high-grade papers.

The more important yellow and orange pigments used in colored coatings include Hansa yellow, lead and zinc chromates, and the molybdated chrome oranges. Hansa yellows are the best in respect to fastness to light, but they are very difficult to disperse properly and so tend to cause variations in color if dispersion or agitation varies in different parts of a run. Lead chromate is the most widely used of all the yellows but it has three drawbacks: it turns dark and loses its brilliance when exposed to sunlight; the greener shades change toward the orange in the presence of alkalies; and it is poisonous. Zinc chromate may be used where greater permanence is desired than can be obtained with lead chromate, but it is considered to be an even more dangerous poison than the lead salt.

For blues of the redder tones the ultramarines are unsurpassed and they work well in any coating mixture. For greener tones the reduced lakes of the Monastral blues are fast becoming important. The toners develop their color strength too slowly to be of value as coating pigments. This type of blue is the newest and most important addition to the colored pigments in recent years. Iron blues must be handled very carefully if they are to be used in coating mixtures. The shade changes gradually toward the green, they become dull in the presence of alkalies, and their high water content makes the desired high solids impossible in deeply colored mixtures.

For greens the phosphotungstate lakes are widely used because of their fastness to light. Chrome greens are not so satisfactory because they tend to change toward a bluer shade in the presence of alkalies.

Reds of the best fastness include toluidine, para, and Lithol reds, which are best used as lakes. In too great strength all three will bronze badly and so tend to appear brownish. Lithol reds make very frothy coating mixtures and, unless extreme care is taken in mixing, a salvy mixture results. For less permanent work turkey red and

scarlet lakes are suitable. Both are bright, clean colors but bleed badly in the presence of alkali, and the scarlet lakes require a strongly alkaline adhesive to prevent its coagulation.

In addition to these pigments there are available all sorts of lakes which may be used singly or in mixtures to produce the desired color. These are made in different ways by the different producers and as a result have properties which make them work quite differently in use. When a satisfactory supply is located it is best to adhere to it, unless trials and price considerations prove that there is a very distinct advantage in a new sample.

Pigments in coatings may be made more satisfactory in a number of ways. For the duller colors it is good practice to tone them with soluble colors; the pigment supplies the light fastness, and the dye contributes brilliance. For pigments which tend to be lumpy or hard a preliminary grinding in a pebble mill is desirable; this prevents color specks in the coating and often increases its tinctorial power enough so that appreciably less of it is needed. In dispersing colors, either by grinding or by ordinary mixing, attention should be paid to their pH values; acidification aids in the dispersion of some. Wetting agents are also of value with some of those which are less easily dispersed in water.

Calender Staining. This method is used with boards and some of the heavier papers, to put a thin layer of color on one or both sides of the sheet. It is more economical than beater dyeing, but the color is likely to " water-spot " and rub off if it is wet.

In this method of application one or more color boxes are arranged on the calenders so that the corresponding rolls are wet with the color solution. This is then transferred to the paper as it passes through the stack, and the pressure so limits the amount applied that the sheet is practically dry when it leaves the calenders.

Acid colors are usually recommended for this type of coloring, but any color of good solubility can be used; those which require much water for solution, or which precipitate easily, will not be satisfactory for deep colors. For the latter it is good practice to color partly in the beater and top on the calender. For absorbent or very slightly sized papers an aqueous solution of the dye is used, but hard-sized papers tend to color streakily; if this happens, some wetting agent may be added to make the dye penetrate more rapidly, or the dye may be dissolved in denatured alcohol.

The fastness to both light and water may be improved by using a suitable mordant in a water box following the application of the color.

Dip Coloring. In this process the sheet to be colored is run over a felt- or rubber-covered roll, the lower portion of which runs in a solution of the color to be applied. The paper is then run between squeeze rolls to remove the excess color solution, and then passed over dryers. The method is most often applied to light-weight papers, such as tissues, but it can be used equally well on heavier papers if they are sufficiently absorbent to take up the color solution uniformly.

Acid colors are usually recommended for dipping, but some of the basic dyes are used for the brighter shades provided conditions permit. In making crepe paper an alkaline adhesive is sometimes added to the color solution to make the paper cling to the steel roll and aid the doctor in producing the creped effect. Under such conditions the use of basic dyes is restricted to those not affected by the alkali.

Unless some sizing agent is applied with the color solution or in a later operation, the final paper will be absorbent. Since no mordant is used in dip coloring the color will bleed when wet.

Color and Control Tests. This section can be subdivided into several groups of tests according to the purpose for which they are designed. Determinations of tinctorial strength and shade are useful for comparing two lots of the same dye or pigment and thus checking deliveries with the standard or original sample. Color matching relates more specifically to the selection of colors which may be used to match a given sample of paper, and also to tests made in the mill when starting a run and making certain the color is right. Fastness tests relate to the effects of such agencies as light, acids, alkalies, and bleach.

Tinctorial Strength. Tests of this sort are usually made as checks on deliveries of the same dye or pigment and are based on preselected standard samples. Numerous methods of testing have been proposed, but none is used exclusively, and each individual probably carries out his own ideas in accordance with the uses and properties of the color.

For dip staining, the dyes may be compared by making solutions of different known strengths, immersing pieces of filter paper or white pulp in them, draining, and air drying. In comparing the dried samples the edges should be trimmed off so that only the central part of the sheet is used.

For dyes which are to be used in the beater the most satisfactory method, though relatively time-consuming, is to prepare a quantity of beaten, sized, and loaded stock, divide it into a number of equal parts, and color these with the standard color and with the sample in amounts both above and below that of the standard. Sheets made from these lots will permit strength comparisons to be made. Special

care must be taken to dry all samples exactly alike, or the test will be worthless.

This test is satisfactory for the pigments which disperse as colloidal solutions, including the phosphotungstate lakes, vat color pigments, and Prussian blues, but in some cases long agitation or beating the color with the fiber is essential to develop its full strength.

Pigments such as the earth colors and metallic salts are not conveniently tested by this method because the great dilution of the stock in making sheets is likely to cause irregularities in retention. Good comparisons and permanent records may be made by preparing coating mixtures colored with the pigments and spreading these on paper. All conditions, especially those of drying, must be standardized and followed exactly. The colors of phosphotungstate lakes do not develop in this test, and it is also unsatisfactory for colors easily affected by alkalies, unless a neutral coating mixture is prepared.

To see whether a dyestuff contains one or more dyes, take a small sample of the powdered product on the tip of a spatula and blow it across a piece of wet, white blotter. Each speck of color gradually dissolves, and the various colors of a mixture show plainly and can be tested by chemical means. If the coloring matters were mixed in solution and evaporated together this test fails. For such cases the dye can be tested by making a succession of dyeings of wool or cotton skeins in the same dye bath. If the dye is a mixture the first and last skeins will differ in shade.

Color Matching. When paper of a new color has to be matched the color man must draw on his experience to decide what colors can be used to give the desired results. He must consider the nature of the fibers and fillers and the properties demanded in the finished paper, and with all these in mind he may make a preliminary test by taking some of the beaten stock which is to be used, adding the colors he wants to try, using known amounts, and making a sheet in some of the customary sheet machines. A comparison of this with the paper to be matched will tell whether he is on the right track, and a second trial on a larger scale, possibly a pound of fiber, will give sufficient information to enable a mill run to be started.

All the larger color houses have laboratories in which such matches are made for their customers, and if problems are submitted to them all the information available to the mill color man should be given. Even under favorable conditions such matches are frequently found to be inaccurate in the amounts of color needed, but they furnish a fair starting point for the mill. If such outside matches are checked in a small beater of a pound capacity it is usually possible to establish

the dye needed within 10 per cent of that finally used. The accuracy is less for pigments because the degree of beating and the suction cannot be duplicated on a small scale.

When the first large beater is colored, a little of the stock may be squeezed out and compared roughly with a bit of the sample which was reduced to pulp with a small amount of water so that none of the color would be lost. Better still, a sheet may be made from the beater stock and compared with the sample; the sheet should be given approximately the same finish that the paper will have.

Color matching for coatings duplicates large-scale operations as nearly as possible. If a correctly proportioned mixture of the pigments and adhesives is prepared and the coloring matters added, small hand-coated sheets or " brush-outs " will give a fairly good indication of the amounts and kinds of color which must be used. For the most reliable results all conditions, as solids in the coating mixture, amount of coating applied, body stock used, drying conditions and temperatures, and calendering, must duplicate those of large-scale operation.

If the colored paper is to receive further treatment, as waxing, oiling, or parchmentizing, the colorist must carry out such treatments in order to be certain that his product matches the sample. If the treatment makes the paper translucent the samples should be compared by both transmitted and reflected light, being sure that the sheets are of the same weight and have the same backing.

In matching colors the nature of the light in which the samples are viewed is very important; a subdued north light is generally considered best, and this should be from a window not affected by reflections from adjacent buildings. Whatever light is selected as a standard should be used for all color work, as the same results cannot be obtained if the source of light varies. The use of one of the so-called daylight lamps affords a constant source of light at any time of the day or night. There has recently been placed on the market the Barkon-Frink carbon dioxide lamp which is said to approximate northern sky light very closely and to be excellent for color matching. Any of these lamps should be used in a dark room for the best results.

In comparing colors the first observation should be decisive as the eye becomes less sensitive by prolonged staring. If doubt exists after the first glance, rest the eyes by closing them or by looking at some distant object, and then make a second comparison. When papers are being examined they should be folded so that their thickness prevents transmission of light; it is the reflected light which it is desired to compare. It is also well to change the samples from side to side, that in the right hand being transferred to the left, and vice

versa, since the relative positions of the sheets have an influence on their apparent colors. A still better method is to place the sample between two of the standard sheets.

For permanent records some method of measuring and recording the color of the sample should be used. A number of instruments are available for this purpose, some measuring the reflectance at various points of the spectrum and others recording it over its entire range. These instruments may also be used for testing and standardizing dyes or color solutions. At present such equipment is rather costly, and the average individual has not the experience to enable him to look at a color curve and tell what to do to correct troubles.

Fastness Tests. The fastness to light of colored papers is composed of at least two factors, that of the dyes or pigments used and that of the fibers composing the paper. Since all the fibers are somewhat affected by light no paper can be considered entirely permanent in color, no matter what dyes or pigments were used. Groundwood is

TABLE 61

Fastness Rating	Fade-Ometer		June Sunlight	
	Not Faded	Faded	Not Faded	Faded
	Hours	Hours	Hours	Hours
Poor...........	..	$\frac{1}{2}$	..	1
Fair...........	$\frac{1}{2}$	$1\frac{1}{2}$	1	3
Good..........	$1\frac{1}{2}$	3	3	6
Very good......	3	6	6	12
Excellent.......	6	..	12	..

the most unstable fiber, and next in order is unbleached sulfite; the bleached wood pulps are much more stable and high-grade rag stock still more so. These facts must be considered in making any tests in order that the blame may be placed where it belongs.

Tests for fastness to light are generally made on a strictly comparative basis, using whatever sunlight is available. Since sunlight varies greatly in intensity at different times of the year and is often not available when needed an artificial light rich in ultraviolet rays is often recommended. This gives reproducible light at any time of the year and is always ready when wanted, but there are times when its records do not parallel those of sunlight.

A comparison of the Fade-Ometer with June sunlight has been made by Chalon and Soderberg,[1] who offer the comparisons and classifications shown in Table 61.

Harrison[5] discusses the factors affecting determinations of the degree of fading of colored papers by light, and the possibility of standardizing such measurements. He emphasizes the variation caused by different light sources and the importance of impurities in the air, the temperature during exposure, and above all the relative humidity of the surrounding atmosphere. Other points brought out are the variations in rating fading according to the light in which the samples are viewed and the impossibility of comparing the fading of two colors one of which bleaches while the other darkens. Many other points of lesser importance are brought out, and attempts to develop standards for fading are detailed.

Fastness to alkalies and acids is occasionally demanded for certain products. It is customary to test papers for this property by placing on the paper drops of 1 per cent caustic soda solution, 40° Bé. silicate of soda, and 0.5 per cent sulfuric acid solution. The drops are not blotted off, but are allowed to dry in the air at room temperature. Fastness to bleach is determined in much the same way by using a dilute solution of calcium hypochlorite. These tests are usually comparative rather than absolute.

All these tests, except for light fastness, may be applied to solutions of the dyes themselves in order to compare them with products which are known to be satisfactory. Such tests often prove that a color sample will be entirely unacceptable and so make more extended trials unnecessary.

Tests for bleeding in water, oil, alcohol, wax, etc., may be made by immersing the colored paper in the medium and noting the time required for a slight tinge of color to be imparted.

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COATED PAPERS

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Although paper has been made for many centuries, the development of coated paper is relatively recent. Its essential feature is a thin layer of mineral matter and adhesive applied to the surface of an ordinary sheet of paper. The chief function of the adhesive is to bind the mineral matter so firmly to the paper that it will not be removed by the pull of the ink during printing or in other uses, but the nature of both ingredients and their relative proportions in a coating have a vital influence on the way the finished paper will print. The coating covers the individual fibers and fills any spaces between, so that when the paper is calendered it has a smooth, even, and continuous surface which takes the fine dots of a half-tone plate much more perfectly than the uncoated paper. Such papers are used for lithographic work, magazine and other printing, and especially for the half-tones in catalogs and other advertising matter. These are usually classed as book papers.

Prior to 1874 coated papers were used for label and lithographic purposes,[1] but they were coated on one side only and were not used for printing fine illustrations for book work. At about that date, or early the following year, the problem came up of printing each side in colors which would retain their brilliancy, and this was solved by making paper coated on both sides. Since then coated papers have been improved to permit better and better printing, and their possibilities along other lines have resulted in the production of numerous special and fancy papers which are used for many purposes, such as box coverings, labels, cigar bands, notebook covers, imitation leather, and wallpaper. These are produced by methods not radically different from those for book papers, and the same general principles apply.

Though coated papers possess advantages from the standpoint of the printer, they also have certain more or less serious defects. The paper is heavy and bulky, and books made from it are wearisome to handle. It has poor folding and bending qualities, and if it is handled frequently its useful life is much shorter than that of uncoated paper. When the adhesive used is nitrogenous the coating may be attacked

by certain insects, and if stored in a very damp atmosphere it may even start to decay. The question of the permanence of coated papers is still an open one, but there is some indication that the coating tends to protect the body stock, especially if this contains groundwood. Documents of permanent value should not be printed on coated paper because of its poor durability, though it is believed that its permanence may be as great as that of medium grades of plain papers. Samples are available which are apparently as good as when made in 1906.

The body stock to which the coating is applied should conform to the quality of the coated paper being made. For papers which must stand much folding or handling, high-grade, long fibers should be used, while shorter fibers may be employed for papers where high strength is not so essential. For certain grades, where neither strength nor durability is of much importance, lower-quality fibers, such as groundwood, may be suitable. In Europe groundwood is often one of the principal ingredients though it is of finer quality than that generally made in this country. A practical limit is set to the use of low-grade stock by the fact that the coating is too translucent to prevent dirty or shivey stock from showing in the finished paper.

Body stock is one of the most important raw materials for the paper coater, and its influence on the quality of the finished paper is much greater than is often realized. Some of the qualities which good body stock should have are regular formation, softness and pliability, high bulk, freedom from fuzz and cockles, uniformity of finish, medium sizing as indicated by the water-penetration test, and freedom from dirt. Regular formation and high bulk are essential if the coated paper is to have uniform finish and good printing qualities. If the body stock is wild or bunchy the coated paper will be more dense in some places than in others; this gives the paper a mottled appearance and so influences the absorption of the printing ink that the printed sheet also shows the mottle. High bulk in the body stock gives the calenders more opportunity to flatten the thick spots without changing their density so greatly from that of the thinner places, so less mottle results.

Softness and pliability are necessary if the paper is to run well over the coater, since a hard, snappy sheet will not lie flat, tends to curl on the edges, and does not take the coating as well. The type of coated paper to be made governs to some extent that of the body stock; lithographic papers, for example, require a harder, stronger body stock than most other types of printing papers. Such papers may be kept from curling too much during coating by moistening the edges on the uncoated side by some mechanical means. Hard papers may also

contain " cockles "; these form hills and hollows which prevent uniform distribution of the coating by the brushes, with resulting streaks in the finished paper. On the other hand, if the paper is too soft it tends to be fuzzy, and each fiber which stands up from the surface of the sheet attracts the coating and forms a small thick place which causes a mottled appearance on calendering. This is particularly noticeable when the coating is heavily tinted, for the color seems to collect around the base of each fiber. Very soft papers are also likely to cause trouble from splitting when printing. Sometimes this can be overcome by means of more adhesive, but other properties will then suffer.

One of the important considerations in selecting a body stock is its sizing, but no general statement can be made as to what degree of sizing is satisfactory or unsatisfactory. The variable and rather unreliable methods of testing for sizing make it impossible to compare the records of different plants, and it is often true that what a coater desires is based on personal opinions rather than on carefully collected data. The sizing necessary is also dependent on the nature of the coating mixture and its ratio of solids to liquids, which in turn affects the rate at which it wets the paper. It is obvious that body stock should be sufficiently sized to prevent it from wetting through immediately, since it would then pull apart before it could be carried through the coating operations. Too slack sizing also tends to make the coating weak unless an abnormally large amount of adhesive is used. This defect is much more serious with glue and starch than with casein. On the other hand, if the body stock is too hard sized the coating tends to lie on the surface and be streaky, and cases are known where it was apparently so hard sized that even twice the normal amount of casein did not prevent picking by the wax and printing tests.

The color and brightness of the body stock used are of importance, and it is best that the color be as nearly as possible like that desired in the finished paper; this will make any brush marks or variations in thickness of coating much less conspicuous. For the brilliant whites now demanded in coated papers it is very essential that the body stock be as bright as possible since any grayness of the body stock will considerably reduce the brightness of the finished paper.

Not infrequently different body stocks require very different amounts of adhesive when the pigments used and all other conditions are the same. With starch this may necessitate raising the starch per 100 of pigment from 22 to as much as 30. Differences are even shown by the two surfaces of the same sheet of paper when they are coated with

the same coating mixture in one operation.   There is no uniformity of opinion regarding.this phenomenon; some claim that it is always the wire or always the felt side which is weak, while others say that on the side which is upward the relative position of the pigments and adhesive is different from that on the under side, because of the effect of gravity while the mixture is sufficiently fluid to settle.[24]

Coating Machines.   The mechanical equipment for spreading the coating mixture on the paper has been developed in several directions within the last few years.   There are now the older, brush-type coaters for applying the coating to one or both sides at one operation; roll coaters in which rolls perform the functions of the brushes in spreading and smoothing the coating; and the " air brush " coater which uses neither brushes nor rolls.
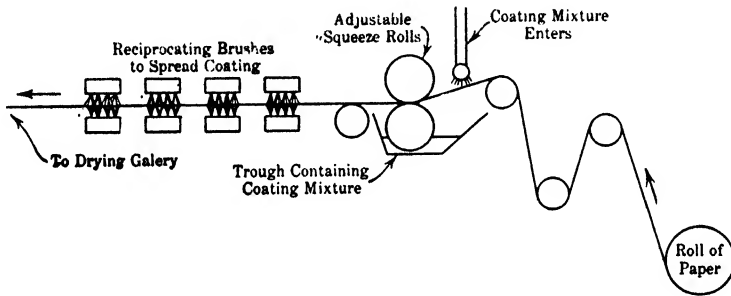
FIG. 47.   DIAGRAM OF BRUSH COATER.

Figure 47 illustrates a brush coater for coating two sides at one operation.   The paper passes over tension rolls and then between adjustable squeeze rolls, which regulate the amount of coating applied.   The coating mixture is delivered in a constant stream to the upper side of the sheet, from which it flows into the trough under the lower squeeze roll.   After rising to a level which allows the roll to carry the mixture onto the under side of the paper the excess returns to the supply tank From the squeeze rolls the paper passes between brushes which work back and forth across its surface, thus bringing the coating mixture into intimate contact with the paper and smoothing it out thoroughly. The first of these brushes is comparatively coarse, but the last, which are generally of badger hair, are very fine, to eliminate the marks caused by the coarser brushes.   After leaving the brushes the paper passes through a gallery heated by steam coils or a current of hot air, and when dry is reeled up ready for calendering.

When only one side is to be coated the mixture is applied by a roller revolving in a trough, to a felt or brush, and from this to the

paper. In the air-brush[20] coater the felt or brush is absent and the paper passes over the roller itself, from which it removes an excess of coating. The web then passes the air brush, which delivers a knife-edged stream of air against it and removes the excess of coating, leaving the rest evenly distributed. The amount of coating is controlled very accurately by varying the velocity of the air stream. This type of coater, which is shown diagrammatically in Fig. 48, overcomes many of the spreading difficulties inherent in brush coaters.
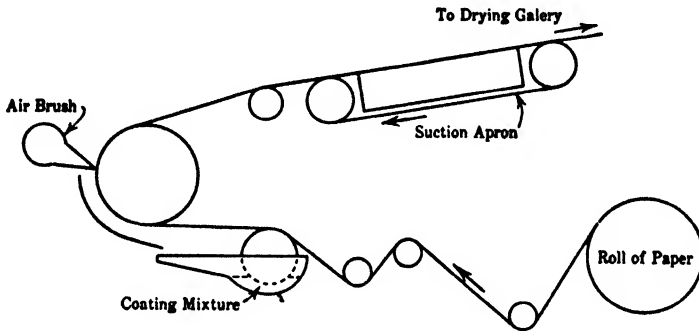
FIG. 48. DIAGRAM OF AIR BRUSH COATER.

Roll coaters are of various types and coat either one or both sides at one operation. Most of them smooth the coating by rapidly revolving rolls which turn counter to the direction of passage of the paper. Some of these coat the paper as a separate operation; others form an integral part of the paper machine and coat the web as it is produced. The latter are used extensively in making the so-called semicoated papers in which the coating applied is very light so that it does little more than fill the depressions and irregularities of the body stock surface. In some coaters of this type the coating is transferred from roll to roll, much after the manner of inking rolls on a printing press, before it is applied to the paper.

A method of coating which serves the functions of both coater and calender has been patented by Bradner.[4] In this the paper to which the coating has been applied is pressed against a solid surface while it is in a highly plastic condition, and when thus dried it takes on the finish of the surface with which it was in contact. This process is capable of producing paper with a high gloss or a dull surface according to the surface of the dryer. The papers are claimed to be of high bulk and opacity and free from mottle. The chief difficulty with this process is that it does not apply coatings to both sides of the sheet.

With most coaters the quantity of coating applied can be varied from a light wash coat to one which amounts to 35–40 per cent of the finished paper, depending on the use to which the paper is put. Each type of coater works best with mixtures of a certain dry content or fluidity, but these are not the same for all types; the best conditions must be studied out for each.

The adhesive in coated paper is chiefly casein, though starch is sometimes used, and also a little glue. Glue was formerly the principal adhesive, but casein displaced it, and even strong efforts on the part of the glue manufacturers have failed to reinstate it. Other adhesives which have been tried or proposed as casein substitutes include soy bean meal and the protein made from it, pectin, alginates, locust bean gum, zein, and synthetic resins of many kinds. Most of these fail to meet the requirements of the industry, either technically or in cost, but the soy bean preparations appear very hopeful.

The proper amount of adhesive varies with different mineral matters and different body stocks. Laboratory trials show that the casein and starch required by various mineral pigments are about as in Table 62. The casein requirements are based on the sealing-wax test, and the starch requirements on actual printing tests.

TABLE 62

Pigment	Adhesive per 100 Pigment	
	Casein	Starch
English clays	10.5–13	14 –17.5
Domestic clays	10 –15	18.5–20.5
Precipitated chalks	15 –25	9 –29
Asbestine	10.5	..
Talc	9.5–12	..
Lithopones	8 –13	19 –20
Satin white	34	76 –86
Titanium dioxide	14	24
Blanc fixe	..	12
Calcium aluminates	4.5–66	..

If too much adhesive is used the paper tends to curl, its color is not good, and the coating is less porous, so that when printed the ink is likely to offset and to mottle instead of lying flat. Such paper also takes a lower finish on calendering than when less adhesive is employed. Printing quality as well as economy therefore indicate the use of as little adhesive as possible, but with too little, the coating will " lift " or " pick " when printed, especially if the ink is tacky. This imposes a

minimum beyond which the adhesive cannot be reduced, but which should be approached as nearly as possible, due regard being had to a sufficient factor of safety to take care of variations in printing inks, pressroom temperatures, etc.   Modern methods of testing the strength of coated papers, and better methods of controlling coating operations, have enabled this factor of safety to be considerably reduced within the last few years.

The influence of the amount of casein on the time required for linseed oil to saturate the paper is well shown in the following experimental data:

GRAMS OF CASEIN PER 100 GRAMS CLAY	TIME IN SECONDS FOR OIL TO SATURATE
10	20
15	37
20	125
25	780–1020
30	Does not penetrate

The mineral matters used in coating paper have changed quite materially in number and importance within the last few years.   Clay is still the most common, but the difference between the fine-grained domestic clays and the relatively coarse English ones is recognized. Satin white is less important, having given place to the fine-grained clays and precipitated chalks.   Blanc fixe continues in use, both alone and with titanium dioxide or zinc sulfide as compound pigments; the dioxide and sulfide are also sometimes used in the commercially pure state.   Other white pigments which find a limited use are talc, barytes, zinc oxide, calcium sulfate, and calcium sulfite.   The qualities of the finished paper depend largely on the mineral matters used, and proper blending of the white pigments makes possible many different effects.

The ultimate test of a coated paper is usually the way it will print, and this is considerably influenced by the minerals as well as by the adhesive.   Each mineral seems to have an individual way of reproducing a half-tone dot, depending on the particle size of the pigment and the rapidity with which it absorbs the vehicle of the ink; hence it is important to select and balance the mineral matters carefully if the desired printing results are to be obtained.

The qualities demanded in a coating mineral are good color, fine particle size, freedom from grit, and the ability to work up into a good, fluid mixture when the adhesive is added.   The color demanded is usually much brighter than that expected of a filler, and the price paid is correspondingly higher.

Besides the two main ingredients in the coating mixture, other substances are often used in smaller amounts for special purposes. Soaps or waxes, either in solution or as emulsions, are added to improve the finish; waxes also aid embossing. Anti-froth oils prevent excessive foaming of the coating mixture, and glycerine or one of its substitutes is added to give the coating increased flexibility. Nearly every manufacturer has some such modification of the regular process which he generally considers a secret, though it often proves to be quite widely known. There is thus a very wide field for chemistry in the coating industry, and it is probably safe to say that it offers more and harder problems than almost any other department of paper making.

Coating Mixtures. The preparation of the coating mixtures has a considerable influence on the quality of the finished paper and on the economy of the process. The materials should be very thoroughly mixed and free from even the smallest lumps, for these cause loss on screening and very small ones pass the screens, make the paper rough, and injure its printing properties. Very complete mixing can be obtained by grinding all the ingredients together in a pebble mill, but such mills are difficult to keep clean and free from decomposing casein.

The amount of water used in a coating mixture is usually governed by the necessity for making it spread without showing brush marks. It should be kept as low as possible in order to aid drying and keep the adhesive required at a minimum. There is also some evidence that mixtures with high solid content give better coated papers. It is generally assumed that the higher the viscosity of a coating mixture the more brush marks it will cause. This is not necessarily true, for cases are known where the higher in viscosity of two similar mixtures spread better and with fewer brush marks than the more fluid mixture. Since the factor which indicates spreading ability is not at present measurable the best that can be done is to depend on viscosity measurements.

The viscosity of a coating mixture is influenced by many different factors, some of which are known, and some not even suspected. It is decreased by adding water or by raising the temperature of the mixture, and it is increased by increasing the ratio of adhesive to mineral matter. These generalities seem to hold for all the common adhesives, though not to the same degree for all; even two starch-containing mixtures apparently may be affected to a different extent.

Viscosity measurements are sometimes very confusing, especially with coatings containing starch, since some of these have decided thixotropic characteristics and measurements made at different time intervals give entirely different answers. Unless this trouble is

known and guarded against decidedly incorrect conclusions may be drawn.

Some of the other variables which cause differences in viscosity are the kind of minerals used, the kind of adhesive, and with casein the kind and amount of alkali used to dissolve it, the presence of wax or oil emulsions, the use of preservative or waterproofing agents, the order of adding the materials when making the mixture, the temperature at which the mixture was made, entirely apart from that at which it is used, and the presence of chemicals of various kinds. Apparently it is possible to modify the viscosity of coating mixtures by adding certain reagents, but it is impossible to be specific because the action of the chemical depends so much on the ingredients of the coating. It is evident that the development of a coating mixture giving the desired character to the paper and at the same time having satisfactory working properties is by no means a simple proposition.

Another factor of importance in a coating mixture is its tendency to foam. Starch mixtures foam least, casein to a much greater extent, and the earlier soybean protein mixtures much more than casein. The foam is of two rather distinct sorts, a coarse froth on the surface and a fine foam, thoroughly emulsified, in the mixture. The fine one is the more serious and may cause bad froth pits in the coated paper unless chemicals are added to reduce the surface tension and change the fine foam to the coarse kind. Avoidance of mechanical conditions which tend to emulsify air in the mixture is also helpful. Why one casein froths more than another is not known, but as the trouble comes and goes without warning it is necessary to use anti-frothing agents as a matter of insurance, when, for the greater part of the time, they are probably not needed.

The finish obtainable on coated paper depends on the materials used as well as the way in which it is calendered. Satin white and very fine-grained clays give the smoothest coating and the highest gloss, ordinary grades of English clay give a lower finish, and blanc fixe takes less polish than either. Precipitated chalks give varying finishes depending on their particle size: the finer the particles the higher the gloss. The greater the moisture in the paper when calendered the higher the finish, but there is a limit to the amount which can safely be present, since too much causes the paper to crush or blacken and its color and appearance are seriously injured. The amount of moisture which will cause this varies with the different coating materials and with the conditions of calendering, so no very definite limit can be set. It must be lower for papers containing satin white than for most others, and it is safe to say that, if the paper contains much

more than 5 to 6 per cent, very great care will have to be taken in calendering.

The finish of paper may be considered as composed of two factors, smoothness and shine, of which only the former is required for good printing. Since a high gloss is both injurious to eyesight and inartistic it would seem desirable to avoid it as far as possible. Dull-finish papers with highly satisfactory printing qualities can be produced by the proper coating materials and by calendering lightly, but as most of the materials which do not readily take a high finish also cause poor printing, it is necessary to use some of the pigments which give a high finish, even in a dull coated sheet.

Dull coated paper may also be made by applying a thin wash coat to a coated and calendered paper. This gives a peculiar velvety surface which takes half-tones beautifully, but is easily marred by handling, a slight stroke with the fingernail sufficing to cause a distinct mark.

The printing qualities of coated papers are influenced by so many factors that an evaluation of any one, or even of their relative importance, is a matter of extreme difficulty. It seems fairly well established that the kind of adhesive and the nature of the mineral matters are of prime importance. This subject is discussed in more detail in Chapter XVII.

Glue. Glue was the first, and for a long time practically the only adhesive used for coating paper, but it is now seldom used in the ordinary grades of printing papers. This is due to the lower price of casein and to its superior ability to make papers waterproof, and less liable to injury from moist hands, which are very likely to disfigure glue-coated papers. Glue, however, is still used for certain products, and papers with very satisfactory printing qualities can be made with it, provided its lack of moistureproofness can be ignored.

Glues come in many different grades, ranging from the poorest bone glues to the highest quality of hide glue. Hammill, Gottschalk, and Bicking[18] found that the amount of glue required to give a coating of satisfactory strength varied almost inversely as the grade of the glue when rated by jelly strength. A medium-grade hide glue could be substituted for casein, pound for pound, whereas more than twice as much of a low-grade bone glue might be needed. High-grade hide glues had even greater strength than casein.

Ground glue is easier to handle than sheet glue, as it takes up water and dissolves much more quickly. In order to avoid hydrolysis and loss of strength it is best to avoid high temperature in dissolving the glue and in storing the solution before use.

Glue for coating paper should be of good color and strength, free from objectionable odor, nearly neutral in reaction, and have a low grease content. Any grease present should be readily emulsifiable to such a finely divided state that it will not cause " eyes " in the coating, but if grease is entirely absent the coated paper may dust on the calenders and take a low finish. A satisfactory test to show whether grease is present in harmful amount or form is made by coloring a fairly strong solution of the glue very deeply with an aniline dye and then brushing it lightly onto white paper. If many eyes form, the glue is to be regarded with suspicion.

The acidity of glue may be determined with fair accuracy by dissolving 1 gram of the sample in 500 cc. of water, adding a few drops of phenolphthalein solution, and titrating with 0.1 N alkali. The amount of acid in glue is quite variable, often running as high as 1.2 per cent (expressed as sulfuric acid), but for sensitive colors it is best to keep it below 0.3 per cent.

The adhesive strength of glue is an important factor in determining whether it can be used economically. It may be determined as described under " Casein."

Lack of moisture resistance in glue-coated papers may be overcome to some extent by using a little chrome alum with glue, the amount ranging from $1\frac{1}{2}$ per cent of the weight of high-grade glue to $3\frac{1}{2}$ per cent for inferior grades. The amount which can be used without injury to the viscosity and working life of the mixture must be determined for each glue. For the same amount of hardening agent, water resistance is increased more with hide glues than with bone glues.

Water resistance may also be improved by treating the coated paper with formaldehyde or adding it to the coating mixture. It is not so effective with glue as it is with casein.

Casein. Casein is a nitrogenous body which is present in milk to the extent of about 3 per cent by weight. It may be separated from milk by the action of acids or rennet, but rennet casein is so difficultly soluble in alkaline solutions that it is almost never used in paper coating. Acid caseins may be prepared by the action of any of the mineral or the stronger organic acids, or the milk may be allowed to curdle spontaneously from the formation of lactic acid. In the early days of casein manufacture its quality was considerably influenced by the kind of acid used, and caseins were usually described by the name of the acid, as " muriatic," " sulfuric," " self-soured." With recent methods of manufacture these differences have almost completely disappeared, and it is impossible to tell the kind of acid used from any tests which can be made on the casein. This has resulted in

much greater uniformity of product and less trouble for the paper coater.

Commercial casein is prepared from milk which has been passed through cream separators. The skim milk is warmed to 49° to 50° C., acid is added, and when the curd has settled the whey is drained off. The curd is then washed with water, drained, pressed to remove as much moisture as possible, shredded, and dried in a current of warm air. The dried curd is then ground to any desired degree of fineness.

These have been the essential operations for years, but modern methods have made a remarkable improvement in the quality of the product by controlling the temperature of precipitation, the pH of both precipitation and washing, and the completeness of the washing. Bell[3] states that if precipitation is made at pH 4.1 the curd has a resiliency and texture which make washing easier. The acid is best mixed with the milk by adding it continuously in a small stream and then subjecting the whole to thorough agitation. Washing seems to be one of the most important factors in producing high-grade casein, and because of the type of curd produced by modern methods this can be done much more completely than formerly. Gould and Whittier[16] have shown that calcium and phosphorus, whether left in the casein because of insufficient washing or added as solvents, tend to lower the adhesive strength of the casein. Phosphorous has more effect than calcium, but it is sufficient in either case to indicate the necessity for very complete washing.

The wet curd is dried in a number of ways, often spread on cloth-covered trays in a drying tunnel. It must be completed promptly so that the curd may have no chance to decompose or mold. Whittier and Gould[32] studied the effect of drying " grain curd " casein for about 5 to 6 hours at different temperatures and concluded that casein dried up to 95° C. was good for coated-paper work. It becomes increasingly difficult to dissolve as the temperature rises, and if dried at 130° it swells but does not dissolve. The solutions with borax also become thicker with increased drying temperature of the casein.

The nitrogen in pure casein was found by various investigators to range from 15.12 to 15.74 per cent; Richmond[26] claims that it is very close to 15.67 per cent. If this is correct, the percentage of nitrogen found in any sample multiplied by 6.38 will give the percentage of pure casein, i.e., free from ash, fat, moisture, and other impurities. Commercial caseins vary quite widely in nitrogen content, according to the amount of impurities and the moisture present when the sample was taken. According to Browne,[8] the average nitrogen content in 19 domestic caseins was 12.74 per cent, so commercial casein may be cal-

culated by multiplying the nitrogen by 7.85. The use of this average factor to calculate the casein in any sample of coated paper or coating mixture may give quite incorrect results. If it were applied to the maximum and minimum analyses for nitrogen in the samples tested by Browne it would show 112 and 92 per cent of .commercial casein respectively. It is evident, therefore, that it gives only an approximate figure for the casein originally taken.

Table 63 indicates what may be expected of commercial products.

TABLE 63

Per cent	Domestic[8]			Argentine[30]		
	Max.	Min.	Avg.	Max.	Min.	Avg.
Moisture...	10.09	5.30	7.74	8.79	4.48	6.06
Ash.......	5.68	2.61	4.15	3.78	3.61	4.03
Fat........	3.86	0.33	1.41			
Nitrogen...	13.10	11.73	12.74			

From the examination of 22 samples Whittier et al.[33] obtained the following results:

Ash varies from 1.86 to 4.58 per cent
CaO varies from 0.03 to 1.53 per cent
Fat varies from 0.00 to 2.25 per cent
pH   varies from 3.37 to 4.76 per cent

The specific gravity of commercial casein ranges from 1.31 to 1.34, and the weight per cubic foot is 38.6 pounds if run loosely into the container or 47.8 if tamped.

The moisture in casein varies with the humidity of the surrounding atmosphere, as is shown by the results of tests on two commercial samples.

PER CENT HUMIDITY	MOISTURE IN	
	SAMPLE 1	SAMPLE 2
40.6	7.27	7.20
47.5	8.27	8.06
52.7	9.13	8.99
62.2	10.53	10.53

This shows that the moisture content quoted in Table 63 may indicate merely the condition of storage of the samples and not an essential difference between the domestic and the Argentine products.

Casein is essentially acid in nature and will not form a solution, or rather a colloidal dispersion, unless some alkali is present. It forms

two series of salts, basic caseinates neutral to phenolphthalein, and neutral caseinates neutral to litmus. The caseinates of sodium, potassium, lithium, and ammonium are readily soluble; those of the heavy metals are insoluble. The alkaline-earth caseinates differ somewhat in solubility. With warm water strontium caseinate gives a solution which is practically identical with one of sodium caseinate. Calcium caseinate forms a white, opaque, pastey mass when soaked in cold water; heating causes immediate coagulation, but if an excess of ammonia is added and heat applied the semi-solid masses dissolve and the solution takes on the usual appearance. Magnesium caseinate is much like calcium, except that it is thin when hot and thick when cold; ammonia acts much as it does with calcium caseinate.

The alkaline substances proposed as " solvents " for casein range from the ordinary inorganic alkalies and alkaline salts to the alkaline organic compounds such as the amines and quaternary ammonium compounds. Those commonly used are ammonia, and the carbonate, borate, and phosphates of sodium. Caustic soda is a good solvent, being cheap and rapid in action and giving good solutions, but it is seldom used because any excess is considered dangerous. Table 64 shows the amounts of a number of the solvents necessary for just complete solution of 100 pounds of casein, and also the quantity equivalent to the caustic soda necessary, assuming that the solvent power depends only on the base present. These figures are averages of many observations made on caseins in use a good many years ago, and because of the improved quality of modern caseins they may be too high for present products.

TABLE 64

Alkali	Pounds Solvent	Chemical Equivalent
NaOH	2.35–3.10	2.35–3.10
NH$_4$OH	3.15	3.45
Na$_2$B$_4$O$_7$·10H$_2$O	14.7	18.9
Na$_3$PO$_4$·12H$_2$O	12.3	12.5
Na$_2$SO$_3$·7H$_2$O	14.0	12.5
Na$_2$CO$_3$	5.14	5.23

With the phosphates the reaction evidently ceases when dihydrogen sodium phosphate is formed; this is confirmed by the fact that the latter salt has no appreciable solvent action even when used to the extent of 50 per cent of the weight of the casein.

Actual use of these solvents brings out certain marked differences of some importance. Ammonia and caustic soda are rapid in their action, even at relatively low temperatures, and are especially useful in dissolving the last traces of lower-grade caseins. Phosphates give thinner solutions, but because of injury to the strength of the casein, as shown by Gould and Whittier,[16] the necessity for their use should be carefully investigated before they are employed. Borax is a reliable general solvent and as it is also a preservative its use is quite common, especially in mixture with other solvents. It has been known to cause trouble by thickening coating mixtures containing satin white, but this may have been due to an insufficient amount. Calcium hydroxide is almost never used in paper coating but is the most common solvent in casein glues and would seem to have possibilities which should be more carefully investigated. It is cheap and gives a thoroughly waterproof coating, but it must be used without heating, which makes it somewhat slow in action. It also seems to cause very bad foaming in the coating mixtures, and the useful life of the mixture is somewhat restricted as it tends to gel, especially if lime is in excess.

Whatever the solvent, an unnecessary excess should be avoided as it is wasteful, darkens the color of the solution, and often causes it to thicken. The full strength of a casein is developed if the alkali is enough to give a solution neutral to litmus. A moderate excess does not injure its strength, but a large excess may, particularly if the heating is too prolonged. Bryson[9] states that the higher the alkalinity of casein solutions the less rapidly they putrefy but the more rapidly they hydrolyze. High alkalinity does not prevent mold growth.

The insoluble matter in well-made casein is negligible in amount, but if the curd was kept too long before drying, and appreciable mold growth took place, the casein may contain white, flaky masses of mold hyphae. This is now very unusual but was formerly quite common. If for any reason the insoluble matter is sufficient to be troublesome on the coaters it can be removed and the good casein made available by passing the casein solution through some form of centrifugal clarifier.

Casein solutions and coating mixtures are likely to spoil, especially in warm weather, and then should not be used because of their bad odor and because the strength of the casein is greatly lowered. Many substances have been proposed as preservatives, and tests have shown that borax, pine oil, terpineols, cresol, artificial mustard oil, sodium othophenylphenate, and mercuric chloride are among the most effective. Of these, borax serves also as a solvent and pine oil as a foam

reducer; if the pine oil is used regularly, no spoilage of the coating mixtures need be feared within any reasonable time.

One of the great advantages of casein in coatings is that it can be rendered so insoluble that the paper will not stick together if it becomes wet. This is usually accomplished by adding formaldehyde or hexamethylenetetramine to the coating mixture. It is best to dilute the formaldehyde very considerably, to keep the coating mixture from thickening. This is influenced by the alkali used in dissolving the casein, the amount of formaldehyde, the temperature at which it is added, and the rate of addition, so that no generally applicable rules can be given. Small amounts of formaldehyde do not cause immediate waterproofing, but the property develops gradually as the paper ages. Hexamethylentetramine can be used in larger amounts and with fewer precautions than formaldehyde but it is generally not so effective. Paraformaldehyde is as effective as formaldehyde, though it requires longer to develop its maximum effect, and it is often found that the coating mixture must be used almost immediately to avoid trouble from continually increasing viscosity.

Formaldehyde was mentioned as early as 1898 by Hall[17] in a process for making a waterproof composition. He recommended dissolving the casein in a suitable alkaline solution, then adding the mineral materials and finally the formaldehyde. Soda was not a satisfactory solvent as the formaldehyde then caused immediate precipitation. This was avoided by the use of ammonia, and enough formaldehyde could then be added to render the solution neutral or slightly acid. The mineral matters were considered to retard the precipitation of the casein and the " setting " of the solution. He recommended about 3.5 per cent of a 40 per cent solution of formaldehyde.

Many other substances are capable of rendering casein insoluble but cannot be used in the coating mixture because of curdling or thickening, though they may be applied after the paper is coated. Moistening the paper with solutions of salts of iron, aluminum, lead, copper, magnesium, zinc, etc., and again drying, will make it so waterproof that it can be washed without injury. Schwartz[27] proposes making casein products by adding to an ammoniacal solution of casein an ammoniacal solution of a compound of copper, tin, zinc, magnesium, etc.; he claims that after drying the product is no longer soluble. It would seem that some such process might be possible in coatings. Bradner[5] claims that a coating is more waterproof if it is made with a casein solution which was treated with chlorine or sodium hypochlorite.

Casein which has been kept too long, especially at summer temperatures, is likely to become infested with worms. These cause deteriora-

tion in the value of the casein somewhat in proportion to the degree and time of infestation. Casein thus affected requires less alkali to give a neutral solution and may lose as much as 50 per cent of its original strength in a year. The best conditions for long storage would approach those of cold-storage plants.

Testing Caseins. The tests which may be applied to casein are of two general classes: (1) chemical analyses for certain constituents, or (2) empirical tests to show its use characteristics. Numerous studies have been made of the methods of analysis and their results,[31,28,32,8] and the conclusion generally reached is that there is practically no correlation between the analytical figures and the working qualities of the caseins in coatings. For this reason the empirical tests are of much more value to the paper coater, and of these the tests for solubility, alkali required, adhesive strength, and viscosity imparted to a coating mixture are the most important. Such tests should be made to conform as nearly as possible to manufacturing procedures in the plants where the casein is to be used, so the following methods are merely suggestive though they have been found convenient in use.

The solubility of the casein and the alkali required may be determined by soaking 50 grams of the casein in 200 cc. of water, adding the solvent in gradually increasing amounts, and warming on the steam bath after each addition. The amount should be started at a point so low that the solution will be incomplete and the reaction acid to litmus. After each increase in solvent the solution should be observed for undissolved material and for its reaction. In this way it is possible to determine the alkali required to give a solution neutral to litmus and to note whether it is complete at this point. If it is not complete the excess of alkali necessary to dissolve the casein may be ascertained by continuing the test beyond the neutral point.

In this test the neutral point is considered to be when blue litmus is turned slightly red and red litmus slightly blue. Though not a particularly sharp change it is usually sufficient for the purpose; if greater accuracy is desired, the pH value after each addition of alkali should be determined by means of the glass electrode. Completeness of solution may be judged by keen observation and experience, or the solution may be diluted, settled, and decanted until the insoluble matter can be collected, dried, and weighed. This is seldom necessary, as there is still the uncertainty as to the importance of any given weight of insoluble matter.

The adhesive strength of a casein, or the amount of clay or other pigment which a given weight of it will hold on the paper, is best determined by a method similar to actual coating operations. In

principle this consists in making a very complete mixture of the clay with water, adding a definite amount of casein, previously dissolved with any alkali desired, and coating paper with the mixture. The test should be started with an insufficient amount of casein and this amount gradually increased until an excess is used. This will give a series of coated sheets ranging from very weak to unnecessarily strong, and when these are properly tested they will show the point at which just enough casein is present.

This test can be made by placing the clay slip in a small container, such as a cup, in which it is mixed with the casein solution. The entire assembly — cup, stirrer, and coating mixture — should be weighed on a balance having an accuracy of 0.1 gram. From the weight before and after spreading a sheet the remaining weight of pigment, and hence the amount of casein solution to add for the next sheet, may be calculated. This enables the entire series of sheets to be prepared from the original weighing of pigment, and any reasonable number of sheets may be spread after each addition of casein. If only one sheet is spread, no appreciable error will be introduced if the same standard amount of casein is added each time.

This procedure must be very carefully controlled if the results are to be of any value. The pigment must be the same in every test; different pigments, and even different kinds of clay, require different amounts of adhesive. The paper on which the coating is spread, and the side of the sheet to which it is applied, must be standardized with care, for variations in the kind of body stock are a prolific source of trouble. The weight of coating applied per ream, the temperature of the coating mixture, and the proportion of water which it contains all influence the results and should be controlled fairly closely. This means that spreading the coating on the test sheets must be accomplished by some sort of mechanical device which will apply a uniform coating of definite thickness; it cannot be done sufficiently well by a hand scraper or a brush.

To indicate whether enough casein is present in a coating, sticks of sealing wax are melted at one end, applied to the coated surface with a gentle pressure, and allowed to cool thoroughly. They are then removed by a quick vertical pull while holding the paper down firmly. The nature of the break between the wax and the paper is then supposed to indicate whether enough casein was used. If the body stock is hard and not easily ruptured a deficiency of casein is indicated by the coating adhering to the wax and parting from the paper. At first the entire coating is removed, but as the casein is increased the area of coating pulled off becomes less and less, until finally it all sticks

to the paper and none to the wax. This is the point which is considered indicative of sufficient strength. If the body stock is soft and punky the fibers usually pull off with the coating and then the test shows nothing regarding the coating itself.

Several series of waxes have been developed for this work, at least one of which is of the nature of sealing wax, while another is composed of waxes with quite different properties.

When using the waxes for control tests it is necessary to correlate picking on the printing press with that on the waxes. If it is found, in general, that the paper will print without picking only if it stands the test with the No. 4 wax, it may be assumed that if the same materials are used and the coating is so made that it does not pick on wax No. 4 it will also print without trouble. With different adhesives the test indicates nothing until the wax and printing tests have again been correlated. The test is influenced by both the kind of pigment, and the nature of the body stock. It is also greatly affected by the temperature as well as by the time the wax is allowed to cool before removal. As a higher temperature when testing by the waxes shows the need for more adhesive, while a higher temperature when printing softens the ink and makes less adhesive necessary, the correlation is again upset.

Since a coated paper must print satisfactorily, it would seem that a printing test as a means of controlling the amount of adhesive would be desirable, but unless it can be made at constant temperature it will give very unreliable results, so that paper which is correctly made for printing at summer temperatures may pick very badly if held in storage and printed during the winter. The whole situation with regard to a strength test for coatings is most unsatisfactory, and a more reliable and conclusive test is urgently needed. Attempts to develop such tests are described by Bekk[2] and by Bradner and Montgomery,[6] but no information is available to show how these check with the printing results.

An important factor in testing caseins for paper coating is the determination of the viscosity which they impart to coating mixtures. The viscosity of the casein solution itself bears no constant relation to that of a coating mixture made from it, hence the test must be applied to the coating mixture. This may be done with various commercial viscosimeters, but the MacMichael has been found very convenient and is not affected by small amounts of coarse matter in suspension, as are some of those which measure outflow time. Metal pipettes, however, are considered sufficiently accurate for mill control tests.[14]

To be of the greatest help in any plant the mixture to be tested should be made up according to its working formulas, hence no definite procedure is outlined. The results are affected by the kind of casein, the kind and amount of the solvents used with it, the nature of the mineral matter, the temperature at which the test is made, etc. If all but one of these are held constant, this test can be used to show variations in any one of these important conditions.

The chemical analysis of caseins is probably a waste of time so far as the paper coater is concerned, but occasionally it may be desirable from the research standpoint. For the greatest accuracy many precautions are necessary, and for these reference should be made to the original papers. For most purposes the following methods will be sufficiently accurate.

Moisture may be determined by drying in a thin layer at 100° to 105° C. for about 2½ hours, cooling, and weighing in a closed container.

Ash may be determined by burning a weighed sample in a silica dish, heating slowly to avoid loss by spattering. Platinum dishes should not be used because of the injury caused by phosphates in the casein. Rennet casein burns out readily and yields a high ash, while acid caseins are much harder to ignite free from carbon.

Fat may be estimated by extracting the finely ground sample in a Soxhlet or Underwriters apparatus with ether and petroleum ether, evaporating the solvent, and drying and weighing the fat. Because of the very dense nature of the casein particles this is a slow and rather uncertain procedure. A more rapid method is as follows: Soak 2 grams casein in 6 cc. water in a small beaker and after about half an hour add with constant stirring 9 cc. of concentrated sulfuric acid (sp. gr. 1.84). Pour the solution into a Babcock skim-milk bottle, and wash out the beaker with 5 cc. water and 5 cc. sulfuric acid. Fill to the base of the neck with dilute sulfuric acid (4 cc. water and 5 cc. conc. H_2SO_4), and whirl in a Babcock centrifuge 5 minutes. Fill with dilute acid, whirl 2 minutes, and while still hot read the fat on the graduated neck. The reading multiplied by 9 gives the percentage of fat in the casein. The secret of this method is in getting the concentration of the acid just right; if it is too strong the fat will char, whereas if it is too weak the casein will not all be in solution and a reading will be impossible.

Nitrogen is best determined by the Kjeldahl method. The factors for converting this to casein have already been given.

Soybean Products. Soybean adhesives have received attention for many years, and efforts have been made to prepare a satisfactory

purified protein and also to use the very finely ground meal. Great difficulties have been encountered in preparing a pure protein, and the early products were extremely variable in quality and mostly unsatisfactory. The processes involved are essentially treatment of the meal, freed from oil by extractions, with alkaline solutions to dissolve the protein, which is then precipitated by acid and dried.[10,12] The process has proved difficult to establish on a controlled basis, and the intermediate steps in the procedure have considerable influence on the product. Meal which is uniform and of the right quality is necessary, so control of the source of the meal is also essential.

The best soybean protein yet obtainable has practically the same adhesive strength as casein and is soluble in most of the alkaline casein solvents. It will usually require a little more water than casein, but the coating mixtures made with it are of about the usual consistency. The points against it are its relatively poor color and its tendency to foam, which appears to be somewhat greater than with casein. Coatings made with soybean protein can be waterproofed with formaldehyde. The product is so new in paper coating that little is yet known about it. Probably it will eventually become one of the important adhesives, and may even replace casein to a considerable extent.

The use of soybean meal as a coating adhesive has been patented by Dunham,[13] who cooks the meal with 4 parts of water and then passes it through a colloid mill to reduce cellular substances to such a fine state that they do not cause roughness in the coated paper.

Albumen. Both blood- and egg-albumen are similar in some respects to casein yet differ from it by losing their solubility if heated to about 75° C. Solutions of either of these may be prepared by stirring the albumen into warm water containing a little ammonia. The temperature should not be above 20° C., and the stirring must be frequent enough to prevent the albumen from collecting and sticking on the bottom of the container. Other substances are also used as assistants in dissolving albumen, as borax or magnesium sulfate. The strength of albumen is very nearly equal to that of casein, 24 to 28 parts of albumen doing the work of 22 to 24 parts of casein.

Coatings prepared with albumen are not so fully waterproofed by formaldehyde as casein coatings, but they may be made washable by heating, preferably in the presence of steam. Mixtures of casein and albumen when treated in this way give coatings which are good for chromo and leather papers because of their capacity to absorb printing ink. Under certain conditions albumen gives a higher finish

to paper than casein does, yet it is seldom used because of its high price and disagreeable odor.

Starch. As an adhesive for coating paper, starch has many good points; it is clean, of good color, without odor, and non-nitrogenous and hence not liable to putrefactive decomposition; also it has good strength and is cheap. The different starches, such as corn, wheat, cassava, and potato, have quite distinct characteristics yet all are sufficiently alike to discuss as a class.

The raw or unmodified starches have no value in coating paper because of the large amount of water required to make them fluid when cooked, and because their solutions do not render coating mixtures thin and free-flowing as do those of casein. Starches may be made " thin-boiling " by treatment with acids, acid salts, or oxidizing agents. The first two methods give products which yield very fluid solutions at concentrations of 20 per cent, or even higher, but they make thick, heavy coating mixtures which need very large additions of water to enable them to spread.

Oxidized starches, which are the ones most frequently used in paper coating, are generally made by treatment with hypochlorite under carefully controlled conditions and are sold as " chlorinated " or " oxidized " starches. A well-made oxidized starch will give a thin, light-colored, solution when 1 part of starch is heated to 80° C., or above, with 4 parts of water; some can even be cooked with 2 parts of water, or slightly less. Such solutions do not thicken greatly on cooling, and they regain their original fluidity if again heated. Many products of this nature are on the market, but they differ slightly according to the kind of starch from which they are made and the details of the treatment given. They also behave differently when mixed with different pigments, and the coating mixtures are sometimes considerably affected by wax emulsions, which may be added to improve the finish of the paper. For these reasons a satisfactory starch can be selected only after trials in the coating formula which it is desired to use; if one does not work well another should be tried. Variations will be found in viscosity and spreading characteristics, but there are also appreciable differences in adhesive strength. When used with the same pigment and tested with the sealing waxes, various commercial starches have been found to hold from 4.55 to 6.25 pounds of pigment per pound of starch, which is considerably less than for casein under similar conditions. With average mill operations it requires 23 to 25 pounds of starch to replace 13 to 15 pounds of casein.

Considerable attention has recently been given to enzymes for converting starches for use as adhesives. Several enzymes are on

the market, some of which are more or less specific for one kind of starch while others work well with numerous starches. Work with one of these on tapioca starch has shown that the important features to consider are the amount of enzyme used, the temperature and time of its action, and the *p*H of the mixture. Since the original starch has more adhesive power than its conversion products, the ideal treatment would be to convert as lightly as is consistent with the physical properties desired in the coating mixture. With the enzyme used in these tests, 30 per cent above or below that found to give satisfactory conversion had little influence on the strength of the starch, though there was a tendency toward lower strength with greater amounts of enzyme. The effect on the viscosity of the coating mixtures was very marked, viscosity decreasing as the enzyme increased.

Increase in the time the enzyme is allowed to act also decreases the viscosity of the coating mixtures but has little influence on strength, beyond the point where satisfactory conversion was obtained. The temperature at which conversion takes place is important provided the time is constant. No action takes place until the starch is gelatinized; above the temperature of gelatinization the rate of action increases up to a certain point and then decreases with further rise in temperature. This results in a lowering of both the strength of the starch and the viscosities of the coating mixtures, followed by a rise in each. This is because conversion takes place best at a certain temperature and beyond this a point is soon reached where the higher temperature inhibits further action of the enzyme. There is also an optimum *p*H for the action of the enzyme, and above and below this the viscosity of the resulting coating mixture is higher. Table 65 gives the best conditions and the safe limits in using one particular enzyme.

TABLE 65

	Best Conditions	Safe Limits
Amount of enzyme, per cent................	0.5–0.6	0.4–0.7
Temperature of action, °F..................	160	157.5–165
Time at best temperature, minutes..........	40	35–50
*p*H value of starch slurry..................	7.5	6.0–7.5

It is plain that with this enzyme the best results are obtained by holding the charge at 160° F. for 40 minutes, after which it should be raised rapidly to a temperature sufficient to prevent any further action. With some of the other enzymes it is recommended that the tempera-

ture be raised continuously and steadily from the gelatinizing point to that at which action ceases. This temperature varies with the different enzymes from about 175° F. to just below the boiling point.

The use of enzymes for this particular purpose is so recent that very little information has accumulated, but it seems a promising field of study for those interested in starch-coated papers. Its economic aspects depend on the relative prices of starch and casein and on the necessary amounts of each. In general, enzyme-converted starch has less strength than oxidized starch, and of the enzyme-treated starches tapioca is stronger than corn.

Coated papers made with starch do not take so high a finish as those made with casein, and this can be only partly corrected by the use of waxes in the coatings. This is apparently not due to roughness of the coated surface for it is smooth enough to take half-tones well. The printed result, especially with color work, is usually not quite so brilliant as with casein-coated papers, and this is often laid to greater porosity of the starch coatings, which permits the ink to strike in to a greater extent. It is difficult to reconcile this with the fact that oil and printing ink are absorbed more slowly by starch coatings than by those with casein.

One of the chief objections to the general use of starch in coated papers has been the inability to make it waterproof. For some purposes this was not of great importance, but it did permit glossy-surface starch-coated papers to be disfigured if handled with moist fingers. It has recently been found that waterproof qualities can be imparted by adding to the starch coating mixture a small amount of some of the urea-formaldehyde compounds. Some sort of catalyst and the application of heat appear to be necessary or desirable. The reaction is also affected by the different types of pigments. The process is so new that it is not yet known whether it will be commercially practicable.

Synthetic Products. Among the synthetic products which have been tried as substitutes for casein in making coated paper are the polyvinyl alcohols. These have three to four times the adhesive strength of casein and give coatings which take very satisfactory finishes. If too little of the alcohol is used the paper has a tendency to dust on the calenders. This adhesive is non-nitrogenous and will not spoil like casein solutions. It is of good color and requires no alkali to make it dissolve.

Clays. No significant distinction between filler and coating clays can be made, since they are of the same chemical composition. The general distinction that coating clays are whiter and of smaller par-

ticle size is not always true, for some of the whiter and finer-grained clays are used as fillers when the quality of the paper demands it. The coarser-grained clays, however, are not so valuable in coatings as they will not give the desired high finish and printing qualities. Lyons[22] classifies coating clays as " coarse " when the majority of the particles are between 40 and 10 microns; " intermediate " when they are between 10 and 2 microns; and " fine " if below 2 microns. For coating paper he considers particle size of more importance than any other factor. The practical lower limit for particle size in clay or other pigment is usually set at about a quarter of a micron; below this there is a definite loss in opacity.

When certain of the English clays are separated into fine and coarse fractions the fines have a better color than the coarse portions, require more casein, and give higher viscosities to the coating mixtures and better gloss to the calendered paper. Present domestic coating clays are considerably finer grained than the average English product, yet require no more casein, so there is evidently something besides mere fineness of particles which influences the casein requirement.

Lyons also states that, of three clays with the same color rating, the coatings made with the finest will show the best brightness and whiteness, but will suffer the most loss of brightness on calendering. Even at that the finished paper with the fine clay will be superior in color to that made with the coarse sample.

The viscosities of clay coating mixtures vary widely with the different clays, but modern methods of testing for coating strength show that the adhesive requirements vary less than was formerly believed. In tests of six clays of quite different characteristics the casein required has varied only from 10.5 to 15 parts per 100 of clay. At least one of these English clays required more casein when the coated paper was dried at 100° C. than it did if dried at room temperatures. The adhesive requirements of several other pigments, including a domestic clay, were not affected by the temperature of drying.

In many coating plants the clay is prepared as a slip or slurry, and then pumped to the point of use. If a high ratio of clay to water is desired some form of dispersing agent is necessary, and among those which can be used are solutions of casein, starch, gum arabic, caustic soda, soda ash, several of the phosphates of soda, including the tetra- and hexametaphosphates, and the sodium silicates. Some of these are impractical because of trouble from spoilage; others are excellent though too costly; but silicate seems to have the desired effect at a very low cost and with few drawbacks. About 0.5 per cent on the dry weight of the clay will render a slurry of about 60–63 per cent

solids sufficiently fluid to pump easily. Most of the other dispersing agents must be used in larger amounts, and some of them, if used in excess, cause the slurry to become thick again. This holds true for large amounts of silicate with some clays, but up to 3 per cent is usually safe.

In selecting clays for coating purposes they should be tested for color and brightness, adhesive required, and coarse matter or grit. Particle size is of great importance, but as there is no simple and rapid method for its determination, it is necessary to resort to an indirect test and measure the gloss of a coated paper before calendering. Other things being equal the higher gloss indicates finer particle size. The next best test is probably a microscopic examination at high power to note the size, form, and uniformity of distribution of particles. This requires considerable experience. Color and brightness should not be measured on the clays themselves, but on coated papers in which the proper amount of adhesive was used with the clay.

There is reason to believe that a study of the base-exchange properties of clays might lead to interesting developments in coatings, but direct evidence is lacking. A more intensive study should also be made of the thixotropic characteristics of clay suspensions and coating mixtures, since this is probably closely related to the flow of the coating and the presence of brush marks. Clay used to be considered an inert material, but it is becoming very evident that it is far from that, though our knowledge is still too incomplete to enable us to predict what it will do in coating mixtures. The problem is one of extreme complexity, but it offers an interesting field for study.

Calcium Carbonates. Precipitated chalk and waste lime mud from the causticizing operation have been used for years in coatings, but chiefly in those requiring only a dull finish. Recently much study has been given to this pigment, and there are now produced, by various methods, grades which were entirely unknown a few years ago. The best of these are superior to English coating clays in brightness, opacity, gloss, ink absorption, and printing qualities, and are practically equal to the lower grades of satin white.

The methods of preparing such products are not yet widely discussed but apparently two general methods are in use: the well-known causticizing process in which soda ash and calcium hydroxide are caused to react, and precipitation of the carbonate from milk of lime by means of carbon dioxide. In causticizing the secret seems to be the proper selection and slaking of the lime and rapid agitation while the reaction is taking place. Relatively low temperatures during reaction are also essential.[7]

In the carbonating process Statham and Leek[29] agitate milk of lime so violently that a fine mist is formed in the presence of carbon dioxide at a temperature of 50° to 60° C. The product is said to be light, non-colloidal, and of the finest possible particle size. Rafton and Brooks[25] pass carbon dioxide at relatively high concentration into the bottom of a draw tube through which the lime slurry passes under conditions of violent agitation and at temperatures between 15° and 50° C. The product is claimed to be colloidal.

Blanc Fixe and Barytes. Both of these are barium sulfate, blanc fixe being prepared by precipitation while barytes is the natural mineral ground and bolted to any desired degree of fineness. The best grades of blanc fixe are made from witherite ($BaCO_3$) by dissolving in muriatic acid, filtering and precipitating with sulfuric acid. The precipitate is washed practically free from acid and marketed either dry or as a paste containing 25 to 30 per cent of moisture. Cheaper grades of blanc fixe are produced as by-products in the manufacture of hydrogen peroxide, etc., and appear to be nearly equal to that from witherite in color and cleanliness. Under the microscope blanc fixe is seen to consist of extremely fine crystals, of very uniform size. If large, irregular-shaped pieces are present it may indicate adulteration with barytes or very careless handling of the solutions before precipitation. Well-made blanc fixe should all pass a 300-mesh screen, with the possible exception of a few tenths of a per cent consisting of small lumps of the blanc fixe itself, which did not break down during the test.

Barytes contains much more coarse matter than blanc fixe, and the particles retained on the screen are angular and quite variable in size. It is also inferior to blanc fixe in color and is seldom used in high-grade papers.

Blanc fixe is considerably brighter than most of the coating clays, but not so bright as high-grade satin white or the zinc and titanium pigments. It has good opacity but is not one of the best pigments for printing, and paper containing it takes a relatively low finish. It is especially serviceable in making dull-finish coateds, to which it imparts a characteristic satiny feel. It is considered superior to clay as an " extender " for colors, both in their manufacture and in their use in coating mixtures. To obtain equal reduction in color intensity, from 2 to 4 parts of blanc fixe will equal 1 part of clay. It is also used extensively in coating photographic papers and in those for recording instruments where the record is made with a metal stylus.

Titanium Dioxide and Zinc Sulfide. These are two of the newer pigments to be used in coatings. Titanium dioxide has a specific

gravity of 3.90 and an index of refraction of 2.55, while the correspond-
ing figures for zinc sulfide are 4.00 and 2.37, respectively. Both of
these serve to increase the opacity and brightness of the papers. They
take a lower finish than the fine-grained clays, but as they are al-
most always used in small quantities with other pigments this is not
a serious fault. Of these two pigments titanium dioxide is the more
frequently used. In addition to these commercially pure pigments
there are numerous compound pigments in which one or the other is
used in conjunction with barium sulfate or calcium sulfate; some-
times both are used as in the case of titanated lithopones.

Some of these pigments do not disperse well in the coating mixture,
and the small lumps make the coating feel rough before calendering
and injure its printing qualities. This trouble can be overcome by
wet grinding the pigment before use.

TABLE 66

Temperatures	Weights of Samples		
	1	2	3
°C	grams	grams	grams
25	100	100	100
50	98.84	98.85	98.55
75	90.74	86.70	87.90
100	74.75	71.95	69.30
125	72.20	69.58	66.95
145	71.13	68.33	65.77
Ignited	60.02	56.87	53.52

Satin White.   Various formulas have been assigned to this pigment;
at first it was thought to be a mixture of calcium sulfate and aluminum
hydrate; later Cobenzyl[11] concluded that it was calcium sulfate and
calcium aluminate; while according to the present theory it is calcium
sulfoaluminate formed according to the reaction:

$$6Ca(OH)_2 + Al_2(SO_4)_3 + 25H_2O = 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$$

This conclusion has been reached by Meyer[28] after a careful study of
the work of Lerch, Ashton, and Bogue[21] on the sulfoaluminates of
calcium and a comparison of their data with the formulas proposed
by Fuchs[15] and Cobenzyl.

Satin white is generally sold as a paste containing about 30 per cent
dry matter. This is an indefinite statement, since the loss of moisture
from satin white depends on the temperature at which it is dried.
This is shown in Table 66 for three different samples which were first

dried to constant weight at 25° C. and then successively at higher temperatures.

When exposed to indoor atmospheric conditions, satin white which has been dried at 75° C. slowly regains part of the weight lost. The rate of moisture loss at 75° C. is also very slow, and as much as a week may be needed to reach constant weight.

It is claimed[19] that paste satin white may be rendered fluid by the addition of small amounts of dry, finely powdered gum arabic and that less than 3 per cent will make it fluid enough to flow freely. Other materials, as some of the sodium salts of sulfonic acids of dinaphthyl methane, have this same effect on some satin whites but not on all.

The preparation of satin white consists simply in mixing alum or aluminum sulfate with milk of lime, but the conditions under which the mixture is made and the subsequent screening and washing have a great influence on the type of product. The alum may be added in solution, as a finely ground material, or in relatively coarse lumps; the last was an early method but is probably seldom used now. The best grades of satin white are said to be diluted, screened through a fine-mesh wire, filter-pressed to the desired degree, and thoroughly washed in the press. Cheaper grades are made by mixing the milk of lime and alum solution at such concentrations that the mixture contains the desired proportion of solids; the product is not screened or washed. Considering these possible variations, as well as the influence of temperature, rate of addition of alum, method of mixing and chemical composition of the lime and alum, it is not strange that satin whites vary considerably in chemical and physical properties as well as in their behavior in coating mixtures.

The chemical composition of satin white, as obtained by analysis, shows nothing about how it will act in coatings. Nevertheless a few analyses of different products may be of interest; they are based on material dried at 140° C. (See Table 67.)

The alkalinity in these analyses is that given by direct titration with acid using phenolphthalein as indicator; it does not necessarily indicate the presence of free lime. Since analysis does not help, the evaluation of satin white must depend on small-scale laboratory coating experiments.

Satin white gives to coated papers a high gloss on calendering and a clear white color, but it is likely to injure its folding properties by making the fold more jagged. If the paper is to calender without becoming dingy it must have a rather low moisture content.

TABLE 67

Constituent	Percentage Present in Sample			
	1	2	3	4
Alumina, Al_2O_3....................	13.13	11.52	14.54	14.15
Calcium oxide, CaO..............	37.38	46.00	44.22	42.77
Sulfur trioxide, SO_3..............	31.98	24.48	29.68	27.43
Sodium oxide, Na_2O....	4.25	1.56	1 52	0.92
Insoluble in acid and SiO_2........	0.36	0.24	...	...
Loss on ignition.....	15 63	24.60	12.40	14.40
Alkalinity as $Ca(OH)_2$...........	22.90	36.80	29.45	30.02

Accessories. Under this heading are included those materials which are used in small amounts or for special purposes and which do not form a principal part of the coating itself.

Soaps and waxes are added to improve the finish obtained on calendering. Such materials include beeswax, carnauba wax, stearic acid, paraffin, Japan wax, white soap, and many others. Many of these can be obtained as ready-made emulsions or they can be prepared by the use of some of the modern emulsifying agents and with the aid of colloid mills or homogenizers. No generally applicable formula can be suggested for all materials, but one of the most useful methods involves oleic acid and triethanolamine as emulsifying agents, followed by passage through a homogenizer. Very stable and useful emulsions can be made in this way. Another very easily prepared and stable emulsion can be made by melting equal parts of stearic acid, paraffin, and Japan wax in about $1\frac{1}{2}$ to 2 gallons of water per pound of wax and then adding about 15 per cent of borax on the weight of the wax and stirring thoroughly.

Such materials doubtless assist in obtaining the high finish desired on glacé papers, but they are probably unnecessary for most printing papers and it is even possible that they may retard the drying of the ink. Their effects should be observed carefully before they are employed too extensively.

Closely connected with this class of materials are those added to prevent frothing of the coating mixture; in fact, some of the substances sold to improve the finish are also claimed to reduce froth. Anti-frothing agents which have been used are widely different in character, as for example, wood alcohol, Turkey red oil, butanol, skim milk, cetyl alcohol, octyl alcohol, and pine oil, and besides those whose composition is known there are dozens of others which are sold under trade names which reveal nothing regarding their make-up.

The relative value of foam reducers can be determined in the laboratory by preparing a coating mixture of the usual composition and dividing it into portions of known weight, one for each of the samples to be tested and one for a blank. The blank is agitated violently in a definite and reproducible manner and the mixture immediately poured into a container of known volume until exactly full, and weighed. To the other portions are added definite amounts of the foam reducers, and the agitation and weighing are done exactly as before. The greater the weight of the container full of the agitated mixtures the less is its content of emulsified air and the more efficient the foam reducer. Short mill trials of foam reducers are almost valueless, since foaming occurs and disappears in a most mysterious manner and it is never possible to be sure whether absence of foam indicates good casein or an efficient foam reducer. The only moderately satisfactory way to try it in the mill is to use it over a considerable period of time.

For softening and increasing the pliability of coated papers it is often recommended that glycerine be added to the mixture, but as a means of improving the folding properties of the paper it is of very doubtful value, at least in amounts up to 2 per cent of the weight of the dry clay in the mixture. In greater amounts it may injure the printing qualities of the paper. Since glycerine slowly evaporates, any effect which it might have would not be entirely permanent. Other softening agents which have been recommended are invert sugars, ethylene glycol, and triethanolamine. These may be useful in certain special cases but they do not appear to be in general use.

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CHAPTER XIV

WATER

E. Sutermeister

Water which is pure, in the sense that it contains no foreign matter of any kind, is never found in nature, so from the manufacturing as well as the sanitation standpoint it must be considered with reference to the amount and kind of impurities which it contains. These may include solid, liquid, or gaseous substances, and they may be either in suspension or solution. Both inorganic and organic materials may be present, and the latter may be derived from decaying vegetation or from minute living organisms. Some of these substances may have a great influence on the quality of the paper; others, which are harmless for this purpose, are decidedly bad if used in boilers. The quality of the available water supply is, therefore, of vital importance in the manufacture of paper and should be carefully considered in locating a mill.

Even when injurious materials are present in relatively small amounts their ultimate effect may be very appreciable because of the large quantities of water used. It is seldom that any accurate records are kept of the amounts employed in the various manufacturing operations, and they are known to vary widely in different mills. Skinner[17] gives in Table 68 the amounts required in making various kinds of pulps. These are not actual operating figures but estimates upon which the requirements of new plants are frequently based. They may be considered maximum amounts, which may be materially less if a mill is designed and operated with water economy in view.

It has been estimated that, in American mills, making linens, bonds, and ledgers from rag stock, the water used amounts to 1000 gallons per pound of dry paper made.[2] For converting pulp to paper on either a Fourdrinier or cylinder machine Skinner considers that 30,000 to 40,000 gallons per ton of paper is a reasonable estimate, but in modern systems where water is carefully conserved much better figures may be expected. For making newsprint Bearce[4] gives the average water consumption as about 15,000 gallons per ton of paper, while one mill with a nearly closed system uses only 2500 gallons. Based on actual results in mills where relatively complete white water utilization has

TABLE 68

GALLONS OF WATER PER TON OF WOOD PULP

Part of Process	Ground-wood	Unbleached Sulfite	Bleached Sulfite	Bleached Soda	Sulfate
Wood preparation....	5,000	10,000	10,000	5,000	10,000
Liquor making.......	....	30,000	30,000	35,000	35,000
Fiber preparation	....	15,000	15,000	15,000	15,000
Bleaching..........	....	.....	30,000	30,000	.....
Machine operation ...	10,000	10,000	10,000	10,000	10,000
Fresh-water showers..	25,000	30,000	35,000	35,000	25,000
Steam and power.....	.....	15,000	15,000	15,000	15,000
Miscellaneous........	10,000	5,000	5,000	5,000	5,000
Totals........	50,000	115,000	150,000	150,000	115,000

been developed, Baker[3] gives the data in Table 69 for excellent and tolerant utilization as reflected in fresh water used per ton of product.

It is evident that no generally applicable figures can be given because its use depends so largely on local conditions, as purity, quantity available, cost of pumping, necessity for filtration, and re-use of backwater, but considering the enormous volumes used and the very effective filter formed by the paper stock it may readily be seen that the problem of water is one of very great importance.

TABLE 69

Product Made	Fresh Water in Gallons per Ton	
	Excellent	Tolerant
Pulp mill, unbleached.....................	20,000	30,000
bleached.............................	25,000	40,000
Paper mill (no stock washing).............	10,000	20,000
Pulp (unbleached) and paper...............	25,000	35,000
Pulp (bleached) and paper................	30,000	45,000
Paperboard...............................	3,000	6,000

Waters may be broadly classified as (1) rain, (2) surface, and (3) ground waters. Rain water, if properly collected, is the purest form of natural water, though it always contains gases and impurities from roofs, products of combustion, etc. Because the amounts available are so small it is of no practical importance in paper making.

Surface waters include those of brooks, rivers, ponds, and lakes. These pick up various impurities according to the nature of the soils

over which they flow, and they are also contaminated by mineral sub-
stances from springs which discharge into them. They generally con-
tain less mineral but more organic matter than ground waters, and
river waters particularly are likely to vary greatly in composition
at different periods of the year. Where the rivers are subject to pol-
lution from manufacturing plants variations are likely to be of much
greater magnitude and frequency. Suspended matter is usually pres-
ent to some extent and in swamp waters a yellowish color is usually
extracted from decaying vegetation. Waters of this type are also
likely to contain plant and animal life which may give them consid-
erable color.

Ground waters are those which have percolated through a consider-
able depth of soil and the underlying porous strata. Those derived
from springs and deep wells are usually clear and colorless but they
contain more dissolved mineral matter than surface waters.

Waters containing small amounts of mineral substances which are
capable of decomposing soap are called soft, while hard waters possess
this property to a marked degree. The most common cause of hard-
ness is the presence of calcium sulfate or carbonate, the carbonate
being much the more general. The salts of magnesium have an even
greater effect, but they are not present so often. The sulfates of
both calcium and magnesium are soluble in water, but the carbonates
require the presence of carbon dioxide to enable them to dissolve as
bicarbonates. This is derived from the air, from the decay of vege-
table matter, or from subterranean sources. Bicarbonates form what
is termed " temporary hardness " since on boiling the carbon dioxide
is driven off, causing the precipitation of calcium carbonate and the
softening of the water. Sulfates cause " permanent hardness " since
they are not affected by boiling.

Qualities Affecting Pulp and Paper Manufacture. Water in paper
making has been considered chiefly as a vehicle for conveying fibers
and mixing them with the other paper-making materials, and very
little real study has been given to its influence on the processes in-
volved, except with regard to a few of its more obvious properties.
There is now some indication that the composition of water, or at
least its pH value, may have a considerable influence on the formation
of the sheet on the paper-machine wire, and doubtless further careful
studies will bring out other important points.

The qualities of water which are generally considered to have an
important influence on pulp and paper making are (1) color, (2)
suspended matter, (3) hardness, (4) presence of iron, and (5) presence
of manganese. Uniformity of temperature and composition are de-

sirable, but, especially with surface waters, little can be done to control them.

The color of water is one of its most important properties, and for high-grade white papers it should not exceed 5 on the platinum-cobalt scale. Surface waters may show all variations in color, from practically colorless through yellow and red tints to deep brown for swamp waters. Red water may be due to iron but more often is caused by decaying organic matter such as tannins or humic acid in colloidal suspension. Such colors are very permanent, and their complete removal can be effected only by chemical treatment followed by filtration. Color from organic matter is likely to be pronounced in summer months because of the growth of algae, and again in the fall and early winter because of the leaching out of color from fallen leaves.

Suspended matter in water is injurious because the mat of pulp or paper fibers forms an efficient filter and retains the dirt in the sheet. Since suspended matter is nearly always colored its effect enhances that of any soluble coloring matter in the water. The amount of suspended matter varies widely, especially in river waters, where rains wash finely divided soil, leaves, and other foreign matter into the stream. Sewage and mill effluents may also contribute an appreciable amount of suspended matter.

Hardness in water is said to be a disadvantage for many pulp and paper-making operations, though it is believed that such statements are not always based on carefully conducted tests. It is claimed[18] that hard water for washing sulfite pulp causes the deposit of calcium and magnesium resinates on the fiber, thus making bleaching difficult. In washing soda pulp, calcium and magnesium salts are precipitated from such water, carrying down coloring matter which is also hard to bleach. Hard waters are also objectionable because of the scale which they deposit when in constant contact with such metal parts as pumps, pipes, and the wet end of the paper machine. The breaking away of this scale is likely to cause trouble, and the frequent use of acid to clean it off the wire materially shortens the life of the latter.

Water which is very hard because of the presence of calcium bicarbonate may also be injurious to sizing, though the presence of calcium sulfate is harmless. For other purposes, as in the boiling of sulfite, soda, or rag stock, or in bleaching, or furnishing a beater, the importance of soft water is greatly overestimated, since the materials employed will immediately harden the softest water. With regard to bleaching it has been proved by Curran and Baird,[8] working with waters of 321 and 186 parts per million of hardness by the soap test,

and with permutite-softened and distilled waters, that there was no appreciable difference in the results.

In making colored papers the quality of the water may affect the results. Carbonates cause precipitation of the salts of iron, tin, and aluminum, which are sometimes used as mordants, and thus reduce their effectiveness. Sulfates have little or no action. Neither carbonate nor sulfate will cause trouble when using acid colors, as the amount of acid used far outweighs any alkali present in the water.

In general it may be said that soft water is desirable but not absolutely essential, since excellent papers are often made with hard water provided it comes up to the other requirements for color, sediment, and low iron and manganese content.

The presence of iron in water is very objectionable in all pulp and paper-making processes because cellulose has the property of absorbing this and other metals from dilute solutions. This results in the yellowing of white papers and the dulling of colored ones, especially light tints. Iron is especially troublesome in the manufacture of photographic papers, particularly if it is present in such form that it may collect in pipes, reservoirs, etc., as such sludge may break away at times and cause endless trouble. It is also claimed to hasten the deterioration of rosin sizing when paper is exposed to light.

Iron may be present in either the ferrous or ferric condition; in ground waters it is usually in solution as ferrous carbonate, while in surface water it is nearly always present as colloidally dispersed hydrated ferric oxide. Ferrous iron may occasionally be present in surface water because of the discharge of trade waste into the streams.

The amount of iron permissible in water for making high-grade white papers is said to be 0.1 part per million, or at the most 0.2 part. West Coast waters,[14] except those of the Columbia River, contain from 3 to 100 times the permissible amount and are usually very corrosive to iron equipment. Since West Coast woods are higher in tannins than the eastern species, iron in the water is especially bad and causes darkening of the pulps made. Unbleached sulfite from this section may contain from 10 to 40 p.p.m. of iron according to cooking and washing conditions, and bleaching changes this to a highly colored condition. The form in which the iron is fixed seems to be fully as important as its amount.

Manganese in a water supply may be exceedingly troublesome — even more so than iron — because of the black oxide deposits which may cause clogging of pipe lines. It is not a common constituent, and its importance has been quite generally overlooked, but it is found in some localities at certain times of the year. There is a

record[18] of a supply containing 1.2 p.p.m. of iron and 0.8 of manganese which caused clogging of pipes and meters within 2 years of their installation. Another water, containing 0.3 p.p.m. of manganese, stained the walls of the filtered-water basin and caused trouble in the washing machines. The permissible amount in paper making is not definitely known, but it is safe to say that manganese should be removed as completely as possible.

Practically all waters, especially surface waters, consume small quantities of bleaching powder, the amount depending upon the source of the water. Usually the loss of bleach from this cause is slight, but if much organic matter is present, as in swamp waters or those largely contaminated with trade wastes or sewage, the loss may be appreciable. A filtered river water of excellent quality was found to require 0.127 pound of bleach per 1000 gallons, while the waste water removed from commercially washed sulfite slush pulp required 0.485 pound.

Water Purification. The methods of purification necessary for a mill water supply will depend on the type of water available and the grade of paper made. For some supplies, screening to remove coarse debris, followed by simple filtration through sand, will make the water satisfactory. Such a treatment removes suspended matter, except that colloidally suspended, and often improves the color and lowers the iron content.

If the water contains considerable amounts of impurities and the requirements of the mill are exacting a more thorough purification process will have to be employed. This will generally include coagulation, sedimentation, filtration, and often disinfection.

The object of coagulation is to make possible, by sedimentation and filtration, the separation of very fine suspended matter and materials causing color. The chemicals used include aluminum sulfate, ferrous sulfate and lime, ferric chloride, sodium aluminate, and chlorinated ferrous sulfate. These react with the alkaline constituents of the water to form hydrous oxides, and if the water is too acid some alkaline material must be added. The amounts necessary to form the floc vary with the nature of the water and its impurities, and each source is a study in itself. Slight turbidity necessitates a greater proportion of coagulant to suspended matter. Sodium aluminate is not adapted to all waters, but may be of value in treating colored waters, which are usually corrosive if treated with alum.

The chemical features of floc formation are probably best controlled by pH regulation, while its physical character depends on mixing. Colored water coagulates best at a low pH, sometimes as low as 4.4, but removal of floc should be followed by a treatment with lime to

reduce corrosion. The requirements for satisfactory floc formation are initial rapid mixing of the water and coagulant followed by reduced velocities and sufficient time for sedimentation. When properly formed, floc is compact, with sufficient toughness and density to settle and filter without breaking up. Poorly formed floc will pass through sand filters or plug them up rapidly.

Manganese may be completely removed by hydrated ferric oxide floc if it is formed above pH 9.0.[11] Zeolite absorption in pressure units is also effective for manganese, while aeration precipitates soluble iron and manganese under certain conditions. If followed by sedimentation and filtration even excessive amounts — 10 p.p.m. or more — may be reduced to 0.2 p.p.m. or less.

The sedimentation basin, to which the water passes after mixing with the coagulant, should be of sufficient size to permit the floc to settle in the time required for the water to pass through. Efficient sedimentation removes coarse and fine sand and coarse clay within 2 hours by natural subsidence; colloidal sediment takes about twice that time.[13] For water treated with a coagulant the usual detention period is from 2 to 3 hours.

The sedimentation problem varies with the turbidity of the water. In some of the mid-western streams turbidity may run as high as 50,000 p.p.m., with an average of 2500 p.p.m., and 6 to 12 hours in an impounding reservoir will usually reduce this to 500 to 800 p.p.m. In well-treated water the turbidity should not exceed 10 p.p.m. It is estimated[9] that each million gallons of water entering the impounding basin will deposit 1.25 cubic feet of sludge containing 10 per cent of solids for each 1 p.p.m. of suspended solid in the raw water.

Filtration, following coagulation and sedimentation, is usually accomplished by passing the water through sand. The types of filters include slow sand filters, rapid gravity sand filters, and pressure filters, with capacities of about 0.06, 2.00, and 2–4 gallons per square foot per minute, respectively. The pressure type requires less space, and the water is pumped directly from the source of supply to the distributing points, but it does not permit as easy inspection of filtering material or as good washing efficiency as the other types.

The sand used should be pure silica, free from loam and acid-soluble material. Specially prepared and graded anthracite coal is also available and in some cases permits longer operation between washes. The coarseness of the sand influences the depth of penetration of the floc and the life of the filter bed. The size of grain in the top few inches is the important factor in filtration, and washing automatically grades it with the finest particles on top. Washing is necessary when the rate

of flow is insufficient or floc is present in the filtrate. Washing by reverse flow should be at the highest velocity compatible with no loss of sand, as any mud not removed reduces subsequent operating time. Sand is sometimes cleaned by treatment with caustic soda, alone or mixed with soda ash. This may be done hot for short periods of time or in the cold for longer periods, and is followed by thorough washing. A treatment with a sulfurous acid solution, weak enough to avoid danger to equipment or workmen, has also been found effective in cleaning sand.[15]

After passing the filters the water should have a turbidity of not over 0.5 p.p.m.

Treatment of water by chlorine or chloramine to reduce bacterial and slime growths is now common practice in mill water supplies. Chlorination before filtration helps keep the filter beds clean and aids their operation, but may cause tastes and odors from trade wastes and algae. Organic materials absorb considerable free chlorine, and pre-chlorination must be varied to meet the conditions of the water; after filtration chlorination will be much more uniform. Chlorine is generally applied at such a rate that the residual after 5 minutes' contact amounts to 0.2 p.p.m., or about 0.1 p.p.m. after 30 minutes. Sterilization is much faster at low pH — 5.0 to 6.0 — than at 8.0 to 8.5. The amount of chlorine used per million gallons usually varies between 2 and 5 pounds.

The ammonia-chlorine (chloramine) treatment permits greater residual chlorine without developing tastes in the water, and allows a longer time of contact under sterilizing conditions. Anhydrous ammonia is commonly used, and the order of addition of the ammonia and chlorine is immaterial. Adequate mixing must be provided, and about 4 parts of chlorine used for 1 part of ammonia. Above a pH of 8.5 the reaction between chlorine and ammonia produces only mono-chloramine, NH_2Cl, but between pH 4.4 and 8.5 dichloramine, $NHCl_2$ is formed; this is the more active sterilizing agent.

The value of sterilization in a paper mill is chiefly for control of slime growth. If the residual chlorine is held at about 0.2 p.p.m., slime growth in newly installed piping is almost completely prevented, though the action is not drastic enough to kill and dislodge slime which was established before chlorination started.

Soft water containing dissolved oxygen and carbon dioxide corrodes iron and steel seriously. Alum increases the carbon dioxide and hence the corrosion, but iron salts and lime neutralize it, and a deposit of scale by alkaline water checks corrosion. With clean, bright iron surfaces pH values between 5.0 and 9.0 are of equal merit in retarding

corrosion.[12] The use of dry, hydrated lime or milk of lime to maintain the proper pH makes it possible to control corrosion very satisfactorily.

Boiler Feed Water. Water which is to be used for boiler purposes should be soft and free from suspended matter, for substances either in solution or suspension will accumulate and form mud or scale. A water which is satisfactory under one set of conditions may be far from suitable for a different type of service, and the determination of the most effective treatment is often a difficult and confusing problem. This is especially true in modern, high-pressure boilers, where the demands are far more exacting than in the older, low-pressure types. These conditions make it impossible to do more than state a few generalities; for more complete details some of the excellent books on the subject should be consulted.

The most troublesome materials in boiler feed waters are suspended solids, which frequently cause priming and foaming, and calcium and magnesium salts and silica, which are the chief scale-forming substances. Sodium salts, because of their solubility, are usually not objectionable except at extremely high concentrations, and not all calcium and magnesium salts are scale forming, though they may cause hardness; calcium chloride and magnesium sulfate are in this class.

One of the most frequent causes of scale is calcium carbonate. This is present as bicarbonate but at the temperature of the boiler is again broken down into calcium carbonate and carbon dioxide. This same reaction takes place with magnesium bicarbonate, and if both are present in the water they will be found together in the scale. The precipitated carbonates are at first loose and powdery but if the boiler is blown off without cooling the flues, the precipitate is likely to bake into a dense, hard scale. Under these conditions magnesium appears in the scale as hydroxide. Calcium carbonate is not so likely to bake onto the plates as the magnesium salt. The following analysis shows the general composition of a carbonate scale; the relative proportions are likely to vary quite widely in different samples, and even in scale from different locations in the same boiler.

	PER CENT		PER CENT
Carbonate of lime	75.85	Silica	7.66
Sulfate of lime	3.68	Oxides of iron and alumina .	2.96
Hydrate of magnesia	2.56	Organic matter	3.64
Chloride of sodium	0.45	Moisture	3.20
			100.00

A certain amount of scale may be formed in boilers even when the water is soft, though in low-pressure boilers it is almost never enough to be serious. The analyses in Table 70 show the composition of a water with a hardness of about 10 to 15 by the soap test, which proved excellent for low-pressure boilers, and also of the scale which formed during its use.

TABLE 70

WATER*

Constituents	Parts per Million	Per Cent of Dry Matter
Silica (SiO₂)	3.8	15.5
Iron (Fe)	0.04	0.2
Calcium (Ca)	3.2	13.1
Magnesium (Mg)	0.6	2.4
Sodium and potassium (Na + K)	4.2	17.1
Carbonate radical (CO₃)	0.0	28.5
Bicarbonate radical (HCO₃)	14.0	....
Sulfate radical (SO₄)	3.6	14.7
Nitrate radical (NO₃)	0.5	2.0
Chlorine (Cl)	1.6	6.5
Total suspended solids	7.4	...
Total dissolved solids	25.0	...

SCALE

Constituents	Per Cent
Moisture and organic matter	17.16
Silica (SiO₂)	35.64
Ferric oxide (Fe₂O₃)	4.32
Alumina (Al₂O₃)	4.28
Calcium oxide (CaO)	30.97
Magnesium oxide (MgO)	5.59
Carbon dioxide (CO₂)	1.40
Sulfur trioxide (SO₃)	0.92
	100.28

* Analysis by U. S. Geological Survey

For high-pressure boilers much purer feed water is required than in the low-pressure types. If condensate return is large, make-up water may be prepared by evaporation and only minor chemical treatment is necessary; otherwise water treatment may be a very serious problem, requiring extreme care in the design and operation of the system. It must be free from scale-forming elements and so treated as to inhibit completely its corrosive, foaming, and embrittling charac-

teristics. Silicate scale is likely to give trouble; the silicates of calcium and magnesium are the most common, but complex sodium aluminum silicates may also form. Silica may be reduced to 3 p.p.m. by floc formed and settled at pH 8.5–9.5 by ferric sulfate and caustic soda.[16]

Zeolite softening after settling, lime softening, and silica removal sometimes gives good results and may reduce the hardness to 1 p.p.m. Disodium phosphate and caustic soda at high temperature precipitate calcium and magnesium almost completely, and with 5 per cent excess of phosphate a hardness of zero by the soap test may be obtained. Processes using new base-exchange and anion-exchange materials are becoming of importance. These replace sodium, calcium, and magnesium ions by hydrogen ions; the effluent contains acid instead of salts and must be neutralized before the water is used.

It is obvious that for modern boilers no simple treatment of the water is sufficient and a combination of several is generally necessary. The effect of the individual treatments of several such combinations is given in tabular form by Powell,[16] who shows the effect of each treatment on the different impurities.

In addition to these softening operations, the water must be subjected to deaeration to remove oxygen and carbon dioxide and prevent corrosion, and so treated that embrittlement of the boiler steel will not occur. This last is accomplished by maintaining the proper ratio of sulfate to caustic in the water, and this varies according to the pressure in the boiler.

Before establishing any purification process a preliminary study of the water should be made, and pilot-plant operation is very desirable.

Water Analysis. The following analytical methods have been taken in large part from " Standard Methods for the Examination of Water and Sewage,"[1] to which reference should be made for more complete details.

Sampling. The sample must be truly representative of the liquid to be analyzed, and if variations are likely to occur, because of periodic contamination by trade waste, a sample obtained by mixing together several portions taken at different times is likely to be more representative than one taken all at one time. The amount required for the ordinary chemical, physical, and microscopical analyses is not less than 2 liters, and for special tests larger quantities may be required.

The samples should be collected in glass-stoppered bottles which have been previously cleaned with sulfuric acid and potassium bichromate, or with alkaline permanganate followed by a mixture of oxalic and sulfuric acids, and by thorough rinsing and draining. The

stoppers and necks of the bottles should be protected from dirt by tying cloth or thick paper over them.

The time which may safely elapse between collection of the sample and its analysis depends on the nature of the water and the tests to be made. No exact limits can be fixed, but it is considered that the analysis should be begun within 12 hours for polluted waters, 48 hours for fairly pure waters, and 72 hours for unpolluted waters. In general, the shorter the time elapsing between the collection of a sample and its analysis the more reliable will be the analytical results.

Turbidity. The turbidity of water is due to suspended matter such as clay, silt, finely divided organic matter, and microscopic organisms. The standard unit of turbidity is that produced by 1 p.p.m. of silica (diatomaceous earth or fuller's earth) in distilled water.

The standard instrument for determining turbidity is the Jackson candle turbidimeter,[20] which consists essentially of a graduated glass tube with a flat, polished bottom, enclosed in a metal case. This is supported over a standard candle so that the distance from the bottom of the tube to the top rim of the candle is 3 inches. Turbidity measurements are based on the depth of suspension required to cause the image of the candle flame to disappear when it is observed through the suspension. The test should be carried out in a darkened room or with a black cloth over the head. An electric light may conveniently be substituted for the candle as it avoids any deposit of soot, but the instrument must then be so calibrated that its readings correspond with those when a standard candle is used.

Color. The "true color" of water is that due to substances in solution, while the "apparent color" is that of the original, unfiltered sample and includes any color caused by suspended matter. A convenient standard for color[10] is prepared by dissolving 1.246 grams of potassium platinic chloride (K_2PtCl_6), containing 0.5 gram of platinum, and 1 gram crystallized cobalt chloride ($CoCl_2 \cdot 6H_2O$), containing 0.25 gram of cobalt, in water with 100 cc. of concentrated hydrochloric acid and diluting to 1 liter with distilled water. This solution has a color of 500, and by diluting in Nessler tubes standards of 0, 5, 10, 15, 20, 25, 30, 35, 40, 50, 60, and 70 should be prepared. These tubes should be of such diameter that the graduation mark is 20 to 25 cm. above the bottom, and of such uniformity that the distance from the bottom to the graduation of the longest tube shall not be more than 6 mm. greater than that of the shortest tube. The tubes should be protected from light and dust when not in use.

The color of the sample is measured by filling a standard Nessler tube to the same height as the standard and comparing by looking

vertically downward through the tubes upon a white surface placed at such an angle that light is reflected upward through the liquid. Water with a color greater than 70 should be diluted before testing, and water containing suspended matter should be filtered, unless the apparent color is desired, in which case unfiltered water should be used.

Nitrogen. This occurs in various forms as ammonia, nitrites, and nitrates, and its determination has been standardized by numerous methods. It is of great importance when considering water from a sanitary standpoint, as its presence in any appreciable amount indicates pollution, but as it has little bearing on paper-making operations, methods for its determination need not be discussed.

Oxygen Consumed. This is determined by heating 100 cc. of the water with 10 cc. of dilute H_2SO_4 and 10 cc. of a standard solution of potassium permanganate, adding 10 cc. of a standard ammonium oxalate solution, and titrating the excess with permanganate. It is considered by some an indication of the amount of carbonaceous matter present, but where pollution, or contamination with trade wastes, has taken place it will also include such materials as nitrite nitrogen, ferrous iron, and sulfides.

As a substitute for this determination it is suggested that a determination of the bleach consumed by the water under conditions of temperature and time similar to those of fiber-bleaching operations would be of much more value to the paper maker. This can be done by adding a known volume of a standard hypochlorite solution and after allowing it to stand for a definite time determining the amount remaining.

Residue on Evaporation. Ignite and weigh a clean platinum dish, and measure into it 100 cc. of the thoroughly shaken, unfiltered sample. Evaporate to dryness on the water bath, heat in an oven at 103° C. or 180° C. for 1 hour, cool in a desiccator, and weigh. The increase in weight gives the total solids or residue on evaporation. The results should be expressed as parts per million, and the temperature of drying should be given in the report.

Fixed Residue. Ignite the total solids in the platinum dish at a low red heat. Cool, moisten with a few drops of distilled water, dry in the oven, cool in a desiccator, and weigh. For the greatest accuracy an electrically heated muffle furnace should be used. The loss on ignition is the difference between the total residue on evaporation and the fixed residue.

Suspended Matter. This may be determined directly by means of an asbestos-lined Gooch crucible or indirectly by calculation from

the difference between the total solids in filtered and unfiltered portions of the same sample.

A test which indicates the paper-making value of water is made by treating a definite volume of the water with enough aluminum sulfate to precipitate all coagulable matter. After the floc is formed, it is filtered through a Gooch crucible or a tared filter paper and the weight of the precipitate determined by difference after drying. The amount and nature of the precipitate indicate whether the water will prove satisfactory without filtration or whether it will be best to treat it chemically before using.

Hardness. The most accurate method of ascertaining total hardness is to calculate it from the amounts of calcium and magnesium found by analysis of the sample. If appreciable amounts of iron or other metals are present these must be included in the calculation. The total hardness expressed as $CaCO_3$ equals 2.5 Ca plus 4.1 Mg.

Titration with a standard soap solution is often employed to determine total hardness, though actually it measures only the soap-consuming power of the water. The soap solution is prepared by dissolving 100 grams of dry, white Castile soap in 1 liter of 80 per cent alcohol. After standing over night the clear solution is decanted and 100 cc. diluted to 1 liter with 80 per cent alcohol. It is standardized against a solution of calcium chloride containing the equivalent of 1.0 gram of $CaCO_3$ per liter. This is done by placing 20 cc. of the calcium chloride solution in a 250-cc. glass-stoppered bottle and diluting to 50 cc. with distilled water which has been recently boiled and cooled. To this the soap solution is added from a burette, 0.2 to 0.3 cc. at a time, shaking vigorously after each addition, until a lather remains unbroken for 5 minutes over the entire surface of the water while the bottle lies on its side. Repeat this test, using 15 cc., 10 cc., and 5 cc. of the calcium chloride solution and finally distilled water alone, and from the results plot a curve showing the relation of various quantities of soap solution to corresponding quantities of calcium carbonate and hence to parts per million of hardness.

In testing water 50 cc. of the sample are placed in the bottle and the test carried out exactly as in the standardization of the soap solution. If magnesium is present a false end point may be obtained. To see if this occurs, read the burette when the end point has apparently been reached and then add 0.5 cc. more of the soap solution. If the end point was caused by magnesium the lather will disappear and the titration must be continued until the true end point is reached.

Temporary Hardness. This is most accurately estimated by determining the alkalinity by titration with $0.02\,N$ acid, using methyl

orange as indicator, both in the original water and again after boiling, cooling, making up to the original volume with boiled distilled water, and filtering. The difference between the two titrations represents temporary hardness and would include iron bicarbonate.

Alkalinity or Acidity. Alkalinity or acidity may be determined by titration with 0.02 N acid or sodium hydroxide, respectively. Indicators for alkalinity include phenolphthalein, methyl orange, lacmoid, and erythrosine, while for total acidity phenolphthalein should be used. Hydrogen-ion concentration in water may be most accurately determined electrometrically by means of the glass electrode, but for most work the colorimetric methods are satisfactory.

Chlorides. The chlorides in water are due to common salt, which may come from mineral deposits in the earth, from wind-borne ocean vapors, or from sewage and trade wastes. Where sterilized water is under consideration the added chlorine is also a factor.

Chlorides may be determined by titrating the water with standard silver nitrate solution, using chloride-free potassium chromate solution as indicator. This shows a faint reddish color when the end point is reached. If the water has a color greater than 30 it should be decolorized by shaking with a little washed aluminum hydroxide and allowing it to settle. The clear portion is then used for the test. The results should be expressed as parts per million of chlorine.

Residual Chlorine. There is no reagent which is specific for chlorine, and the usual test with orthotolidine measures oxidizing agents. Colors similar to that given with chlorine may also be given by ferric and manganic compounds, organic iron compounds, lignocellulose, algae, etc., and as these supplement that due to chlorine the result often indicates more chlorine than is actually present. If chlorinated water contains less than 0.3 p.p.m. of iron or 0.01 p.p.m. of manganese the color developed in the orthotolidine test may be considered as due to chlorine or chloramine.

In testing the sample it should be warmed quickly to 20° C. (but not over 40°) by rotating in an Erlenmeyer flask in a boiling water bath. To 100 cc. in a Nessler tube add 1 cc. of the orthotolidine reagent, place in the dark, and allow the color to develop not less than 5 nor more than 15 minutes. Compare with standards by looking down through the tops of the tubes. Permanent standards may be prepared with copper sulfate and potassium dichromate.

Iron. Iron may be present in both the ferrous and ferric states. In ground waters it is usually in the ferrous condition and combined with carbonic or sulfuric acid or with organic matter. After exposure to air it is often present as a colloidal hydroxide. Silt-bearing waters

may contain much iron in suspension, while waters contaminated with sewage effluents and manufacturing wastes contain various forms of iron of different degrees of solubility.

Total iron may be determined on the material obtained in the test for " residue on evaporation," or a separate sample of 100 cc. of the water may be evaporated to dryness and ignited at a low red heat. If the water contains silt, evaporation should take place in the presence of 5–10 cc. of concentrated hydrochloric acid. After cooling the ignited residue add 0.8–1.0 cc. of 3 N hydrochloric acid, warm on a water bath, and wash the solution into a 50 cc. Nessler tube. Dilute to 50 cc., add 3 drops of 0.2 N potassium permanganate solution, and then add 5 cc. of potassium thiocyanate solution. Compare the color produced with that from solutions of known iron content similarly treated with thiocyanate.

Manganese. The determination of manganese may be made colorimetrically if the water contains less than 10 p.p.m., but if more than this is present it may be preferable to use a volumetric or gravimetric method. The amount of water used should contain not more than 0.2 mg. of manganese. Add to it 2 cc. of nitric acid (concentrated acid diluted with an equal volume of water), and boil down to 50 cc. Precipitate chlorides with silver nitrate in slight excess, and filter. Add about 0.5 gram of ammonium persulfate crystals, and warm the solution until the maximum permanganate color is developed, which usually takes about 10 minutes. At the same time prepare standards containing 0.2, 0.4, 0.6 cc., etc., of a standard manganous sulfate solution in about 50 cc., and treat them in exactly the same way as the sample. Transfer sample and standards to Nessler tubes and compare the colors at once.

The standard manganous sulfate is prepared by dissolving 0.288 gram of the purest potassium permanganate in about 100 cc. of distilled water, acidifying with sulfuric acid, boiling, and just discharging the color with a dilute solution of oxalic acid. After cooling and diluting to 1 liter, 1 cc. of the solution contains 0.1 mg. of manganese.

White Water. Closely connected with the water-supply problem and even more with that of stream pollution is the question of the re-use of white water. This term includes the water from paper machines, pulp grinders, and other operations which do not load the water with impurities which entirely prevent its use. It would not include any waste liquors or washings from pulp mills, or the spent bleach and washings from bleaching operations, though these are most serious factors in stream pollution and also contribute their share toward fiber losses.

The amount of fiber and filler lost during the different pulp and paper-making operations seems to vary quite largely in different mills, and there is not even much uniformity of opinion regarding the losses which are permissible under good operating conditions. Carlson[5] found as average figures for several Swedish mills a loss of fiber, etc., calculated on output, as follows:

	PER CENT
Mechanical mills	5–6
Sulfate mills	2.2
Unbleached sulfite	2–3
Bleached sulfite	4
Cheap printing and news	11.3–14.8
Sulfite papers	3.7–6.4
Rag papers	2

The Committee on Waste of the Technical Association of the Pulp and Paper Industry[6] concluded that the maximum allowable losses, based on paper or pulp production, were:

	PER CENT
All long-fibered stock (kraft, sulfite, etc.)	0.5
Mixed long and short fibers (book, bond, etc.)	1.0
Largely short fibers (news, chip board, etc.)	1.5

As compared with these they estimated[4] the average loss throughout the industry, divided according to grades, to be:

	PER CENT
Wrapping	5
News	7
Tissue	10
Board	10
Book	15

More recently Baker[3] has tabulated the percentage fiber loss in mills with relatively complete white water utilization as in Table 71.

No one method for utilizing white water can be given as the best for all mills. Each mill is a study in itself, and many suggestions as to the best methods to apply under any local conditions will be found in the annual report of the Waste Committee of T.A.P.P.I.[7] The only general principle which can be applied is to recover the water with the most solids and allow that with the least to go to waste. The heavier white water can be used in the beaters or on the paper machines, while the lean water can be utilized to some extent in shower pipes. It has been demonstrated that properly designed showers can handle water with 2.5 to 3.0 pounds of stock per 1000 gallons without trouble,

and one tissue mill is using it with 15 to 20 pounds. Clogging of showers is usually due to slime growth rather than fibrous stock, and for such trouble the chlorine and ammonia treatment is most effective.

Since it is not yet general practice to re-use all the white water some method of recovery for suspended solids is usually employed. How this is handled depends on the nature of the suspended matter as well as on local conditions. For long-fibered stock some method of filtration is recommended, while for short fibers, especially if much filler is present, sedimentation methods are probably best.

TABLE 71

	Per Cent Loss	
	Excellent	Tolerant
Pulp mills, unbleached....................	1.00	1.75
bleached..............	1.25	2.00
Paper mills, no stock washing..............	1.00	1.75
Pulp (unbleached) and paper..............	1.50	2.25
Pulp (bleached) and paper................	1.75	2.50
Paperboard..............................	0.75	1.25
Book mills, filler loss in percentage of filler furnish	20.00	30.00

Filters of the rotary type operating on soda fiber will allow from $\frac{1}{2}$ to 1 pound of suspended matter to go to waste with every 1000 gallons of water. This includes all matter coagulable by alum, and microscopic examination shows that it includes almost no fibers of any length, while its color also indicates that it has no paper-making value. Similar filters on sulfite give practically the same loss, but if white water containing filler is added to the stock the loss will increase very materially, but only with respect to the filler, as the fiber loss seems to be practically constant for a given filter and type of operation. Recovery of filler is better with short-fibered stock than with long fibers such as sulfite. In one case where paper-machine white water was applied to a filter handling soda poplar fiber, the stock discharged contained from 11.5 to 15 per cent of clay, while the waste water from the filter showed only about 2 to 2.5 pounds of suspended solids per 1000 gallons, of which only about a quarter of a pound was fiber. Calculated to the basis of the amount of fiber put over the filter this loss of fiber amounted to only 0.35 per cent.

Sedimentation methods as applied to white water from paper machines running loaded papers give very variable results depending on the type and size of equipment and the care with which it is

operated.   If it is of ample size for the flow passing through, the waste
water discharged should be nearly clear and very low in suspended
solids; if it is run beyond capacity it may cause very little saving.
With save-alls of the inverted-cone type, handling water from book
paper machines, the flow to the save-all was found to vary from 5
to 42 pounds and the overflow from 0.15 to 10.3 pounds of solids per
1000 gallons.   Because of other variable conditions the lowest inflow
did not correspond to the lowest waste.   It is Baker's opinion that
an efficient save-all should reduce the fiber loss to less than 1 pound
per 1000 gallons of effluent.   As he believes the water consumption in
a paper mill should be not over 20,000 gallons per ton of product the
fiber loss would be not over 1 per cent of production.

TABLE 72

Type of Plant	Gallons per Ton of Product	Per Cent Loss as Suspended Solids
Sulfite pulp	1800–45,500	0.6–1.67
Bleach plant	39,000	0.40
Kraft pulp and paper	32,000	1.20
Groundwood	15,620	0.08
Book paper	4,700–48,000	1.11–5.76
Newspaper	29,700	1.27
Tissue	7,014–67,380	0.44–1.00
Writing	32,100	1.03
Board	2,144–22,500	0 40–1.90

White waters from paper machines usually contain enough alum to
insure coagulation, but in some cases the addition of alum, or alum and
alkali, may increase the rate of settling sufficiently to pay for the extra
cost.   In more recent practice where alkaline fillers, such as calcium
carbonate, are used the white water is not acid and coagulation may
not take place so readily.   When coagulation is slow or insufficient it
is possible that the addition of small amounts of certain active sub-
stances may promote it.   The Sveen process[19] makes use of about 0.1
per cent of glue, based on the dry stock present, and also mentions
casein, soap solutions, and rubber latex as active agents.   These are
found to have their greatest effect immediately after addition and for
best results subsequent violent agitation should be avoided.   Not
enough is known about the action of such small amounts of materials
to make generalizations safe.

   In any sedimentation process it is customary to return the thick
stock to the beaters or machines while the overflow is used for shower

pipes or goes to waste. The return of such materials with their accompanying chemicals, such as alum, may necessitate some readjustments of the furnish to the beaters. Considerable alum has been known to be saved by re-use of white water.

Stream Pollution. The question of stream pollution is becoming of more and more importance, but it can be only briefly mentioned here. The final result depends on many factors, and about the only ones which can be controlled by the mills are the amounts and character of the wastes which they contribute.

From records of some of the better-operated mills Baker[3] quotes the figures shown in Table 72.

Even this does not tell the whole story, for organic matter in solution is not included in these figures, though it is often more serious than fiber losses from the standpoint of pollution.

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CHAPTER XV

TESTING WOOD PULP

E. SUTERMEISTER

Both producer and consumer of wood pulp are today more dependent on tests which show its quality than they were ten years ago. This is because paper qualities must be held within narrower limits, and many more grades and more special products with peculiar properties are being made. There are also the special requirements for dissolving pulps, the necessity for accurate moisture-testing methods, and the need for tests to evaluate pulps produced experimentally.

Complete details of methods cannot be given here; for these, the original papers must be consulted, but attention is called to the essential facts and to sources of error and means for their avoidance.

Moisture in Wood Pulp. Official rules for weighing, sampling, and testing wood pulp have been issued by a joint committee of the American Paper and Pulp Association, the Association of American Wood Pulp Importers, and the Technical Association of the Pulp and Paper Industry,[41] and the last organization has embodied them in an official standard method.[60] From these sources the following abstracts have been taken.

The wet or gross weight of the shipment, from which the air-dry weight is to be calculated, should be determined (a) by railroad weight of the entire car lot where the tare weight of the empty car was determined by actually weighing; (b) by weight of the entire car lot as certified by an official weighing bureau issuing weighmaster's certificate of weight; (c) by the sum of the truckloads weighed on accurate, tested scales during the loading or unloading; or (d) by multiplying the actual number of bales or rolls in the shipment by the average weight of the bales or rolls weighed and sampled.

The method of sampling depends on the kind of pulp and the place at which the sampling is done. The strip method, which takes a strip 2 to 3 inches wide across the entire width of the web coming from the machine, is suitable for sampling, at the pulp mill, wet machine pulp or pulp coming from drying machines in continuous webs. One sample should be taken for each ton of wet pulp or for each fifth roll or bale of dry pulp. The shipping weight must be determined at the

time of sampling, and if the pulp is stored before shipping the test must be made by the methods to be used at the receiving point.

The strip method as used at the receiving point varies slightly with the pulp being handled. For double-press, wet machine pulp, not hydraulic pressed, a strip 2 to 3 inches wide should be cut through the center of the sheet across the machine run. For unpressed lap pulp a 2-inch strip is cut through the center, alternately long and short way of the lap and cutting half way through. For both products sampling should be continuous at the rate of one strip for each ton of wet pulp, and all strips from a shipment should be cut the same width.

For roll pulp the strips should be 2 to 3 inches wide and cut across the entire face of the roll. The strip from the second layer and four strips located at least 1¼ inches further in constitute the sample from each roll.

The strip method gives high results with hydraulic-pressed pulp, for which the wedge method is recommended. Using a templet with an angle of about 9° with its point in the center of the lap, cut a sample half way through the lap. For each of four laps the sample would be based on each of the four edges in succession, going around clockwise. If the pulp is baled, 20 per cent of the samples should be drawn from the middle lap, 40 per cent from the lap half way between the outside and the center, 35 per cent from the lap next to the outside, and 5 per cent from the outer surface of the outside lap.

No method involving opening the bales can be used at the docks because transportation companies refuse to handle any not rebaled as perfectly as at the original point of shipment. In such cases the boring method is usually employed for both rolls and bales. The samples are taken by boring to a depth of 3 inches with a special tool which cuts a disk about 4 inches in diameter. The disks are removed and 10 of them taken as the sample from that bale as follows:

> One disk second sheet from the wrapper.
> Two disks 1 inch deep.
> Three disks 2 inches deep.
> Four disks 3 inches deep.

Each bale sampled shall be bored but once, and the holes in five successive bales shall represent a portion extending diagonally across the bale. The first hole is to be at the corner, the edge of the cut being 1 inch from the edge. The second shall be half way between the first and the center of the bale; the third shall be at the center; the fourth half way between the center and the corner; and the fifth in the opposite corner in a position corresponding to the first.

For roll pulp the first hole is to be 2 inches from one end, and those in succeeding rolls spaced one-fifth of the distance across the roll, traveling toward the opposite end. The disks are selected as in the case of bales.

Baled shredded pulp may be sampled with a special tool similar to a cork borer, spacing the samples as with baled sheet pulp, boring to a depth of at least 4 inches, and using the entire sample. An optional method is to break open the bales and take grab samples of about a pound from points 4, 8, 12, 16, and 20 inches, respectively, measuring from each of the three exposed surfaces.

The number of samples from a shipment should be at least 5 per cent of the bales, but never less than 15 bales. With rolls at least 10 per cent should be sampled, and, where possible to determine, the same proportion of outside to center rolls should be maintained as coming from the machine. All samples must be from sound, intact bales or rolls taken from different sections of the entire shipment.

The samples should be placed at once in a metal can with a tight-fitting cover and the net weight obtained as soon as possible. If delay between sampling and weighing is unavoidable the edges of the cover should be sealed with friction tape or similar material. Weighing should be done on scales sensitive to 0.1 per cent of the maximum load, and the dried samples should be weighed in cans as soon as removed from the oven.

Drying should be done within a temperature range of 210° to 220° F., and should be continued until two successive weighings at least 3 hours apart check within 0.1 per cent of the wet weight. The entire bulk of the samples selected must be dried out for the test.

The boring method is not accurate for pulp which has been stored in a dry place for some time. Under such conditions the moisture decreases more rapidly on the outside than in the center, and the loss in weight of the bale does not keep pace with the decrease in moisture shown by the samples. Retests on such pulp nearly always show a greater net weight of air-dry pulp than do the original tests, and the seller of the pulp is correspondingly favored. According to Brainerd,[3] this cause for error is well known in Europe. To minimize it he recommends that the first sample be taken from the sixth sheet of the bale and that the number of disks from the other three depths noted in the official method should be 1, 1, and 6, instead of 2, 3, and 4.

Color. Color comparisons of bleached pulps were formerly made against standard samples, but such standards were impermanent, it was impossible to compare pulp sheets of different surface texture, and comparisons varied with different light sources.

An early attempt to correct some of these faults was made by the Sulfite Pulp Committee of the Technical Association of the Pulp and Paper Industry,[39] who used disks filled with plaster, toned with different proportions of potassium chromate, and numbered arbitrarily from 75 to 100. The disks were supported on bearings side by side so that all could be rotated simultaneously at high speed, and the pulp to be compared was cut into disks and fastened to the faces of the plaster disks. Comparisons were made while the disks were rotating and strongly illuminated by one or more daylight lamps.

This method was rapid and fairly satisfactory where one grade of pulp was being tested, but the disks were difficult to duplicate, and as the grades of bleached pulp increased in number many could not be matched against the standard disks and too many of the standards were needed to accommodate all variations in color and brightness.

Landes[26] modified this method by making all the disks of white plaster and pasting on sectors of paper of different sizes, colored yellow or green, or both. This was claimed to be more satisfactory than the original procedure, but still suitable only for routine comparisons.

More recently many photoelectric instruments for the measurement of color have come into use, and most of them can be employed for pulps. These include spectrophotometers which record the reflectance of the sample by monochromatic light over the visible range from about 400 to about 700 mμ and other instruments in which the light is restricted to a narrow band of wavelengths by means of filters. Both types compare the reflectance from the sample with that from a standard — usually a block of magnesium carbonate or a freshly prepared surface of magnesium oxide. According to Lewis,[29] it is easy to duplicate readings with photoelectric instruments within 0.1 per cent, but the standard magnesium carbonate may easily be off by 0.5 to 1.0 per cent.

These instruments are relatively simple to use, but interpreting their records in terms of visible color involves lengthy calculations which cannot be gone into here, but which will be found in various textbooks, or in " A Study of Photoelectric Instruments for the Measurement of Color."[17] When photoelectric instruments are used for such simple work as the testing of bleached pulps one can soon judge from the type of curve whether one pulp is definitely redder or yellower than another, and especially whether there are appreciable differences in brightness. This information will often tell whether a pulp can be used to produce paper of the desired brightness, and so the use of unsuitable pulps can be avoided.

If it is assumed that the color of the pulp as received carries through into the finished paper, it is compared as soon as the samples are air-dry. If the color of the pulp when completely free from soluble impurities is desired a small sample should be disintegrated in distilled water, agitated for at least 5 minutes at about 0.5 per cent consistency, and then made into a sheet, distilled water being used for this also. For slush pulp, plenty of time must be allowed for impurities in the fibers to diffuse out. The use of water other than distilled often degrades the color of the pulp very appreciably, even though the water may appear clear and colorless.

Fiber Size. Fiber size, especially length, is a factor of much importance in paper making, but until recently the only method available for its study was by microscopic measurement with a callibrated micrometer eyepiece. This involves making slides from very dilute suspensions, so that individual fibers may be well separated, and extreme care is necessary to avoid loss of fine material. At least 200 fibers should be measured, and short fibers and fragments must not be overlooked. This method is too slow for use as a control test, but if properly carried out it is a valuable research method.

Since 1930 numerous empirical methods of separating pulps into fractions according to length have been described. Among the first in this country was the use of a small diaphragm screen with a series of plates of standard screen wire, backed with heavier wire.[52] Jones, Alexander, Ross, and Johnston[20] have described a fractionating instrument in which the stock passes through a series of units arranged in cascade, and containing standard wire screens of 14, 28, 48, 100, and 200 meshes. Each unit contains an agitator, and at the end of the run the fibers in each are collected, dried, and weighed. Brainerd[4] has described Clark's classifier, in which the screen rotates instead of agitating the stock.

The major problem in obtaining significant and reproducible screen classification has been to make the fibers present themselves to the screening surface sideways instead of end-on. This has been done by giving the dilute suspension a high velocity over the screen plate with the direction of flow parallel to the screening surface. Two screens which have proved satisfactory are the Canadian Forest Products Laboratory screen[20] and the Bauer-McNett.[24] Clark's classifier also appears to be a useful instrument. In any of these, duplication of results demands exact duplication in every detail of construction and operation.

The most obvious use for these fractionating methods is in groundwood production, for it has been proved that the freeness test may

vary widely without appreciable change in the bursting strength of the test sheets, and that better evaluation is obtained from fiber size distribution tests. In chemical pulps it has been found that coniferous sulfite may contain up to 15 to 20 per cent of material fine enough to pass a 65-mesh screen and that the amount of this has an important influence on the quality of the pulp. This fine material is largely ray cells; it requires much more bleach than the rest of the pulp, is much poorer in color, and contains most of the pitch. Since its amount is influenced by the methods of chip preparation, cooking, washing, thickening, and bleaching, a measurement of its quantity is very desirable.

Fractionating methods should also be useful in studying beating and jordaning. A little evidence along this line has been presented by Kress and Brainerd,[24] who used it in studying the action of a laboratory beater. In such work it must be remembered that shortening the fibers is not the only change caused by beating which affects its paper-making value. Brown[5] separated the long fibers on a 60-mesh screen, made them into sheets, which he then cut up fine with a guillotine cutter. This cut pulp was repulped and separated as before into short and long fibers. The original shorts, as compared with those made by cutting, were 100–300 times slower and the shrinkage was 3–5.5 times as great. The burst was 3–4 times as great, tear 4–9 times, and porosity in seconds per 100 cc. from 100–1300 times as much. From his results on unrefined, bleached sulfite and " super alpha " Brown concludes that: (1) slowness increases as fiber length decreases; (2) porosity and shrinkage are not affected by fiber length; (3) length has a great influence on formation and tear; and (4) shortening the fibers reduces the burst.

Freeness or Drainage Rate. " Freeness " and " slowness " are terms which indicate the rate of drainage of water from the fibers while they are being made into paper. They are at opposite ends of the scale and can be defined only in terms of some definite instrument or set of conditions. Freeness tests are widely used in controlling groundwood manufacture and the beating of fibers in preparing them for the paper machine, but they are also of value in pulp testing to show its rate of change during a definite series of beating operations.

An excellent discussion of freeness testers has been given by Clark,[7] who states that Klemm was the first to measure the degree of beating with the sedimentation tester, in which the volume of stock was noted after it had drained under specified conditions. Skark considered this of very doubtful value for slow stock, and he developed a tester to

measure the total volume of discharge at consecutive time intervals. Both of these give a very rapid discharge of water at first, followed by a slowing down which is more or less rapid according to the condition of the stock.

The next step was to use two discharge openings of different sizes, placed at different heights in the discharge funnel. This allows the first sudden rush of water to be separated from that which discharges more slowly. With very free stock most of the water flows away at the first rush, while with very slow stock the drainage may be so slow that almost all will go through the smaller and lower opening. The principle of the divided discharge is used by the Schopper-Riegler, the Green, and the Canadian testers. Boehm[2] has made the Schopper-Riegler instrument more sensitive for extremely free stocks by increasing the size of the bottom orifice, making the volume of the pulp chamber 5 liters instead of 1, and using stock of 5 per cent consistency. The early Williams tester, and also the 50–50 model, use the divided-discharge principle, though in the latter the orifices are in the bottom of the funnel and differ only slightly in height. The Williams precision tester, however, goes back to the older method of measuring the time of drainage.

To obtain consistent and comparable results from any instrument of the divided-discharge type it is of great importance that: (a) the ratio of stock to water be uniform; (b) the temperature of the stock mixture be always the same; (c) the apparatus be level; (d) the stock mixture be stirred under definite conditions; and (e) drainage be started before the stock begins to settle. The uniformity and size of openings in the wire cloth or perforated metal used to separate fiber and water are also of importance.

According to Skark the factors influencing the outflow of water in his type of tester are: (a) fineness of the fibrous material; (b) the amount used; (c) the amount of water; (d) the surface of the screen and its fineness; and (e) the height of the liquid.

In using any of these instruments, very slow stock may be classed as free if the fibers are beaten or ground so short that many of them pass through the retaining screen.

Physical Tests. These tests are designed to show the paper-making qualities of pulp; they include the three operations — beating, making sheets, and applying tests to the latter. Since neither beating nor sheet making can exactly duplicate mill operations, laboratory tests cannot give an exact measure of the finished paper, but if the pulps are tested by a carefully planned procedure any that are markedly different will be easily detected, and with experience and careful ob-

servation it is possible to predict with fair accuracy how the pulp will behave in use.

The strength of a pulp usually signifies that of sheets made from it, and as the methods of testing such sheets are fairly well standardized the problems involved are those in beating and sheet making. Probably the first attempt to make such strength tests in this country was that described in 1915,[59] in which the beating was carried out in a pebble mill and the sheets made by dipping on a hand mold. Since then much study has been given to such methods, particularly those relating to the preparation of the stock for sheet making, and the number of devices to accomplish this work has increased enormously until it now includes pebble mills, rod mills, Lampén mills, laboratory beaters, kollergangs, Jokro mills, and refiners resembling jordans. The original pebble mills had certain shortcomings, but it is by no means certain that the newer devices have overcome all of these, or that they have not substituted others which are equally serious. The situation has now reached the stage where it is hopeless to expect that stock preparation for testing can ever be so standardized that the majority of stations will use the same equipment. To make comparisons of different plants possible this would be very desirable, but for comparative purposes in any one plant it is by no means necessary.

Whatever method of stock treatment is employed, the fibers must first be uniformly suspended in water. Where small samples of 50 grams are used this can be done without much difficulty by soaking the pulp in water, rubbing it between the hands; and finally stirring vigorously with a stout glass rod. The English standard procedure is to disintegrate 24 grams of pulp in 2000 cc. of water, for 25 minutes, using a special apparatus with an agitator running at 3000 r.p.m.[40] This vigorous treatment causes a certain amount of beating or hydration, especially in pulps which have not been dried. American practice[68] for the 400-gram samples used in the beater treatment is to disintegrate in 10 liters of water for 10 minutes with a stirrer running at about 1728 r.p.m.

For determining the unbeaten or initial strength of the pulp these methods are reasonably satisfactory, but breaking up by hand is not so certain to reduce the stock to a perfectly uniform condition, while the English method very definitely causes an increase in strength. For many purposes the unbeaten strength is unnecessary, but it does give a base to show the effects of small amounts of beating, and for experimental pulps and special studies it is quite useful.

Pebble Mills. When strength tests were introduced there was no laboratory beater which would give even approximately uniform re-

sults, so a pebble mill was tried. The mill first used was a porcelain
jar with an outside diameter of 8.75 inches and a volume of 4.52 liters.
This contained 195 flint pebbles weighing 4320 grams, and the fiber
charge was 50 grams of air-dry pulp, dispersed in water at a consist-
ency of 3 per cent. At first pulps were beaten for a fixed period and
the bursting strengths of the sheets compared. It soon proved de-
sirable to make a series of beatings at different time intervals and to
apply other tests, such as tear, fold, tensile, and shrinkage. In this
way the beating curves show how the different strength factors develop
with increasing beating and give a much better picture of the quality
of the pulp.

The 50-gram charge of these small pebble mills will make a dozen
sheets, 8 by 8 inches and of about 50-pound basis weight, $25 \times 38 - 500$
sheets, which is more than enough for all the tests usually desired. In
spite of the convenience of these small jars, a larger size as recom-
mended by Genberg[14] is probably more widely used. These are 11¼
inches in diameter and 13⅝ inches long, inside dimensions, and take
a charge of 100 grams of air-dry pulp, 2000 cc. of water, and 1780 cc.
of pebbles. For making a beating curve, removal of samples at inter-
vals during the beating treatment was recommended, but it proved
impossible to withdraw accurate samples and the change in the charge
altered the rate of beating for the remainder.

Pebble mills have advantages and disadvantages for this type of
work. They are relatively inexpensive, easy to operate and keep
clean, and when used under standardized conditions give good repro-
ducibility of results. The time required to make a complete beating
curve is rather long, and it is frequently claimed that the stones lack
uniformity and that ash in the pulp sheets due to the wearing away of
the stones and the jar causes serious errors. The most serious ob-
jection is that all jars do not treat the fiber equally even when used
under exactly the same conditions; it is therefore necessary to deter-
mine the proper conditions for each jar by comparison with a master
jar, which should be kept for that purpose only. There seems to be
no way to calculate the proper charge of fiber, stones, and water for
a new jar, and its determination by trial and error is a serious task.

Trouble from ash in the pulp seems entirely unnecessary if proper
pebbles are selected and the charge correctly proportioned. The
original work was done with Belgian flint pebbles, and records prove
that their loss in weight never amounted to more than 0.3 to 0.5 per
cent over a period of 8–10 months of daily use. Repeated tests of
pulp beaten in the small jars have shown very little ash — from 0.3
to 0.5 per cent for a beating time of 3 hours — so it would seem that

high ash in the pulp is due to poor proportions of fiber, stones, and water, or more probably to the use of pebbles other than flint. One such case is known where pebbles from a local seacoast gave exactly this trouble.

Much study has been given to pebble mill beating and to attempting to overcome some of its difficulties. Moore[32] recommends a bronze jar with steel balls instead of pebbles. He claims greater reproducibility and no ash. Bronze balls did not prove satisfactory. Hall and Woodson[15] used a metal jar with bronze balls 1 inch and 1½ inches in diameter. These shortened the fiber more than pebbles but were considered fairly satisfactory because the strength curves were very similar to those with pebbles, though in somewhat different position on the chart. Peterson, Jeffrey, and Maughan[42] compared flint pebbles with porcelain balls and found the latter to give more uniform bursting tests, though the time to reach the maximum was greater. At the peak of the strength curve higher burst and tear values may be expected with porcelain balls. The balls wore differently, due to varying hardness, and for 100 hours of work a charge of about 4600 grams of balls lost 310 grams in weight. The ash in the pulp for a beating time of 80 minutes was about 1.9 per cent.

Morgan[35] compared several methods of beating and found duriron balls so brittle that they were liable to break if lifted and allowed to fall in the jar. Rods covered with relatively hard rubber chipped badly on the ends. In another paper[36] Morgan states that heavy balls tend to slide rather than fall. Peterson and Kolesinskas[43] studied the effect of weight of porcelain-balls charge on the strength of the beaten pulp and found that increasing its weight and the number of balls increased the time required to reach the maximum, and that this was lower than with fewer balls. Tear and freeness decreased with increase in weight of pebble charge. Peterson and Makara[44] give data on the variations of the pulp charge in the pebble mill; Simmonds and Baird[56] compare the use of a pebble mill, a rubber-lined mill using lead balls, and a 20-pound beater.

All these studies are of value, but all involve so many variables that they do little to establish any standard procedure. Probably the best that a mill laboratory can do is to choose the conditions which seem most practical and then direct its efforts toward correlating the results with actual mill beatings. Once the test procedure is established, all details must be followed with great exactness. Another important point is that in developing the beating curve samples should be taken early in the cycle and less attention paid to the maximum strength. Few papers are made under conditions which develop

the full strength of the fiber, and experience has shown that beating is more rapid in pebble mills than in mill beaters, hence the first part of the beating curve is of more importance than the maximum point.

Laboratory Beaters. In America a common appliance for preparing pulps for strength tests is a laboratory beater. Several types are available, but the most favored is the Niagara type, usually known as the Valley beater,[66] in which the pressure of the bed plate against the roll is controlled by a lever and weights. This is capable of beating more nearly like large beaters than any other equipment in general use, but it is sensitive to small changes in design, materials of construction, condition of the roll and bed plate, etc. Beaters in different laboratories do not usually give the same results, and even the same beater varies from time to time according to the sharpness of the knives. Since beaters have been on the market they have been made with iron, monel, stainless steel, and bronze in the tackle, so concordant results cannot be expected from the units now in use.

For good results the beater must be in good condition and certain precautions observed. To sharpen the roll bars a handful of fine abrasive is sprinkled into the stock and circulation continued as usual; finally feather edges must be removed by means of a file or emery cloth, leaving the rest of the bar surface perfectly flat. Knives and bed plate must be kept free from resin, as even a small amount causes important differences in the results. The bed plate must balance freely, and its recess must not become clogged with pulp. In charging the beater only well-disintegrated stock should be used and the bed plate should be down when it is added. A good description of the beater, its furnish, and operation is given by Rothchild, Lundbeck, and Cable,[51] and also in the T.A.P.P.I. standard method.[68]

A complete beating curve is usually made from one charge by sampling at intervals. This is accurate enough if only a few samples are taken, but Moore and Willets[88] found it unsatisfactory for a large number because circulation was slowed down, or even completely stopped. They also doubt that the beating tackle can be kept sufficiently uniform to give duplicate results. It has been noticed that at constant density some pulps circulate more rapidly than others in the beater. This is important, since the work done depends on the number of passes under the roll, but it is not always taken into account. Some users correct for this by adjusting the amount of stock and water until the rate of circulation is always the same.

A beater charge is usually 360 grams of bone-dry pulp, and such factors as degree of disintegration, ratio of stock to water, temperature, and timing require as close control as with the pebble mill.

The Valley beater can be made to give widely varying ratios of cutting to gelatinization by changing the consistency of the stock and the weight on the bed plate. This aids beating investigations where it is desired to duplicate mill conditions. If the mill-beaten stock is made into sheets and completely evaluated for strength factors, and some of the same untreated fiber is then beaten in the small beater, conditions can be so adjusted that practically the same type of sheet will result. If the bursting and tensile strengths are equal to the mill-treated pulp, but the tear is low and the percentage of fine fibers high, too much cutting is being done, and the cure is to raise the consistency or lessen the weight on the bed plate and beat for a longer time.

Other Beating Methods. In Europe the Lampén mill is quite widely used. This consists of a hard bronze ball, machined and ground to a diameter of 132 mm. and weighing 10 kg., in a revolving metal casing with a maximum diameter of 191 mm. A charge consists of the equivalent of 24 grams bone-dry pulp, disintegrated and brought to a consistency of 3 per cent. The mill runs at about 300 r.p.m., and to establish a beating curve treatments equivalent to 1500, 4500, 9000, 13,500, 18,500, 36,000, and 72,000 revolutions are suggested.

This mill is not generally used in this country, and the writer has had no experience with it. It is stated[40] that in the early stages of the beating the ball may be thrown to the periphery of the mill and held there by centrifugal force, thus doing no beating. "Hammering" of the ball because of a clot of fibers may also take place. Both troubles require attention to detect and cure, so the mill apparently needs careful supervision. The action of the Lampén mill would not seem to correspond with mill beating and refining operations which employ sharp-edged bars, but Edge[13] and Harrison[16] have found it capable of giving results which could be interpreted in terms of large-scale operations.

Several laboratory units of the jordan type have been proposed for testing purposes. The "stock-maker"[34] consists of a conical plug with bars on the outside, which rotates in a conical casing lined with bars. The distance between the two is regulated by a micrometer, but the construction is such that they can never come closer than a definite minimum distance. The time required for beating for a complete strength curve is a matter of 2 to 5 minutes depending on the fiber used; this is an advantage or a disadvantage according to the point of view. The machine suffers from most of the failings caused by the use of sharp-edged bars, and there is reasonable doubt as to the reproducibility of results over a considerable period of time.

A laboratory kollergang has been proposed for stock preparation[9,10] and is in limited use. The procedure involves the usual disintegration of the pulp and then its treatment in the kollergang. There is some reason to suspect that gelatinization takes place during disintegration, and cutting in the kollergang. According to the facts presented by the designer it seems to have excellent possibilities, but its use is not yet general enough to permit final judgment.

At best the beating of pulps for strength testing has no entirely satisfactory solution. If correlation with mill equipment is more important than reproducibility between units and over long periods of time, the beater is probably better, but if reproducibility is paramount the pebble mill is more satisfactory.

Sheet Making. To make acceptable sheets for testing, six operations must be standardized: (1) preparing a uniform pulp suspension; (2) removing a representative sample of the proper size; (3) forming a uniform sheet; (4) couching; (5) pressing; and (6) drying.

Several types of sheet machines are available, and from a study of five, using stocks ranging from unbeaten to highly beaten, Doughty and Curran[12] concluded that if the center area of the sheets was used they were all of about equal uniformity. If the entire area of the sheets was considered, the small, round sheets were the most uniform. Slow pulps showed less difference between machines than unbeaten fibers, and no one machine could be chosen as best for all stocks.

After very careful study of pulp-testing methods made in England[40] a device giving round sheets about 6 inches in diameter was developed. This has been adopted as standard in Great Britain and with slight modifications in America also.[69] To enable results to be duplicated closely, everything in its design and use has been subordinated to accuracy, and it is not considered entirely suitable for rapid control testing because of the time required to make and dry the sheets, the space occupied by the large number of drying rings required for continuous operation, and the glazed finish imparted to one side of the sheet. It is claimed, however, that after a little experience, and considering the need for fewer sheets because of their greater uniformity, the time required is little, if any, more than for other sheet machines. For a description of this apparatus and its operation, reference should be made to the two publications cited; they are too detailed to be of value if abstracted.

Because of its cost, its relatively recent introduction, and the objections just mentioned, few of these standard sheet machines are used in this country. Its place is taken by numerous other machines, mostly of the rectangular type, which may not be accurate enough for

exacting reference work but are sufficiently good for control tests. In selecting a machine a number of points should be considered because of their influence on sheet qualities. The water leg should be at least 36 inches long with a quick-opening gate valve and a water seal at the bottom. When no pulp is present this should permit complete drainage of the volume of water used in 5 seconds or less. A water supply pipe, entering under the grid, should allow rapid filling of the water leg and deckle box. The latter should be higher than normal to permit greater dilution of the stock and better sheet formation. To prevent loss of too much fiber a wire of 80-mesh or finer should be used. This has far more influence on sheet properties than is usually realized, and if much is lost the pulp may be quite incorrectly evaluated. Some form of stirrer, moving slowly up and down, should be used in the deckle box to aid sheet formation, and the valve should be opened very soon after its removal in order to prevent reclotting of the fibers.

After the sheet is formed it is couched from the wire with either felts or blotters. Blotters are preferred for accurate work, but the number required when many tests are conducted makes felts preferable for control work. These may introduce unknown errors due to filling up with mineral matter, fine fiber particles, and especially slime growths, and if used they should be washed often and their porosity kept as nearly uniform as possible. The pressure applied in couching is important, and attempts have been made to standardize it by passing a heavy roller back and forth over the felt or blotter, but a weight which gives good results on lightly beaten sulfite may easily crush and spoil a sheet of beaten soda poplar fiber.

Pressing is usually done in books of 5 to 10 sheets between the felts or blotters, and when blotters are used it is often done in two stages with fresh blotters and higher pressures in the second stage. The type of press is immaterial provided pressure is uniform over the entire sheet. The pressure applied is very important since it affects the density of the sheet and its strength; to some degree high pressure at this stage is equivalent to longer beating. At low pressures the sheet properties are more affected by pressure variations, so some definite amount between 150 and 200 pounds per square inch of sheet area is recommended; once established, it, and the time it is applied, should be closely adhered to.

Besides the method of drying sheets described in the T.A.P.P.I. standard, there are others which are simpler for control work. One is to strip the wet sheet from the felt, place it on the surface of a polished, steam-heated cylinder, and hold it there tightly by means of a felt

until it is dry. Contrary to air drying without tension, this gives uniformly smooth sheets, but they have only about two-thirds of the strength of those allowed to shrink during air drying. Prior[45] claims that drying at 60° C. is without effect on the strength of the sheets and has designed a drum, heated by carbon-filament lamps, against which the sheets are held for 15 minutes.

Tests Applied. Testing pulp sheets follows in general the methods applied to paper and requires the same conditioning at constant humidity and temperature. Prior cuts the conditioning time to 15 minutes by placing the sheets in front of a fan. Besides determining the ream weight and the shrinkage on drying, tests are usually made for bursting, tearing, folding, and tensile strengths. The ream weight should be nearly constant in order to avoid correction in the strength factors; such corrections are unreliable for tearing strength, and even more for fold. Shrinkage measurements vary greatly according to the method of drying, the maximum being shown by sheets which are air-dried slowly, without restraint. Unless the method of drying is very carefully controlled and is stated in the report any figures for shrinkage are misleading.

In addition to the customary tests those for density (weight per unit volume), opacity, stiffness, and absorbency are of importance when the pulp is to be used in certain grades of paper. Other tests have been devised and applied locally for special purposes, particularly in research problems, but they have not received very wide recognition.

Schafer and Carpenter[53] claim that the potential strength of ground-wood is not shown by the usual methods applied to sheets made on sheet machines. They prefer to make boards under carefully controlled conditions and then apply static bending tests. Kress and Bialkowsky[23] describe an instrument to measure the swelling of fibers when they are first compressed and then moistened with the liquid whose effect is to be studied. Brown[6] measured what he called " flowbility," which is the volume in cubic centimeters occupied by 1 gram of the pulp in 1 liter of water after standing 15 minutes at 70° F. Before pouring into the liter graduate the suspension is shaken gently while exposed to a vacuum of at least 15 inches of mercury. " Springback " is the increase in thickness on releasing pressure from a mat of wet pulp which was pressed at 125 pounds per square inch. It is expressed as the percentage of the pressed thickness. Both these tests are said to be closely related to important manufacturing conditions. Seborg, Simmonds, and Baird[55] report on further studies of Brown's " springback " and its relation to other properties.

Bleach Requirement. In reviewing the methods developed for determining the bleachability of pulps — also known as " hardness," " degree of cooking," etc. — Karlberg[2] includes: (1) direct methods using hypochlorite; (2) colorimetric methods in which the incrustants in the pulp develop colors in the presence of reagents; (3) direct lignin determinations; (4) indirect lignin determinations, involving the quantitative estimation of certain radicals, as CH_3; (5) acetylation methods, and (6) oxidation methods with reagents such as hypochlorite, nitric acid, potassium permanganate, bromine, and chlorine.

Only those methods which bleach to a standard color with hypochlorite are actual determinations of bleach requirement, but all depend on the presence of non-cellulose constituents in the pulp, and the results obtained are closely related and more or less accurately convertible one to the other. The factors for such conversions vary with the method employed and the type of pulp tested. Those given by Johansson[18] and Wiles[70,61] are based on single-stage bleaching with hypochlorite and cannot be expected to predict very accurately the requirement by modern multistage bleaching, especially if direct chlorination and intermediate alkali washing are included. The chief use of such tests is in indicating the uniformity of the pulp produced, and for this they serve admirably.

Hypochlorite Methods. A typical method using hypochlorite is described by Seborg,[54] who bleaches a series of 15-gram samples in 2-quart jars with amounts of bleach both above and below that which is expected to be sufficient. The stock consistency is 2 per cent, the temperature 40° C., and agitation is continuous until starch iodine gives only a light blue color which persists for 5 seconds. After washing thoroughly with clean water, sheets are made, pressed between blotters, air-dried, and the color determined.

Another method is to add an excess of bleach and, after treating under standard conditions for a fixed time, to determine the remaining bleach. This assumes that all pulps bleach to the same color in the same length of time, which is not true.

These tests should check commercial single-stage bleachings of the same pulp reasonably well, but variations of 1 to 2 per cent of bleach, based on the fiber, may be expected because of differences in consistency, water, variations in process control, etc. If plant operations are on a multistage basis the agreement will be much less close. In any case the testing procedure should duplicate as nearly as possible the conditions under which the pulp will finally be bleached.

Bleaching tests of this sort require too much time, but their results are convincing because bleached samples are actually produced for

demonstration and comparison. They are probably most useful in research and in mills which handle a number of grades of pulp for bleaching. They are not rapid enough for control tests in pulp mills, for which some of the oxidation methods are more suitable, but they serve well to establish the relation of such oxidation methods to actual bleach requirements.

Permanganate Methods. A quick estimate of bleachability by means of permanganate was proposed as early as 1922 by Johnsen and Parsons,[19] who treated 10 grams of pulp in 225 cc. of water with 25 cc. of 1.0 N permanagnate solution, maintained the mixture at 25° C. for an hour, determined the permanganate remaining, and calculated that consumed.

Wiles[70] claims that the permanganate method is equally applicable to all grades of pulp and that its results can be easily converted to chlorine number, bleach required, etc. He defines the permanganate number as the cubic centimeters of 0.1 N KMnO$_4$ used up by 1 gram of the oven-dry pulp under specified and carefully controlled conditions. He recommends that 1 gram of the pulp be weighed in the oven-dry condition and disintegrated with a measured amount of water. To this are then added water, 0.1 N KMnO$_4$ solution and 4 N H$_2$SO$_4$ in such amounts that the permanganate is always $N/300$ and the acid 0.133 N. For pulps of average bleachability 25 cc. of permanganate is used, while for hard-bleaching pulps 40 cc. may be added. The reaction is allowed to continue exactly 5 minutes at 25° C. after addition of the permanganate, and vigorous agitation is kept up with a glass stirrer. At the end of this time the reaction is stopped by adding 5 cc. of 1.0 N potassium iodide solution, and the liberated iodine is titrated by 0.1 N sodium thiosulfate solution. The permanganate number of the pulp is then:

$$\text{cc. } 0.1\ N\ \text{KMnO}_4 - \text{cc. } 0.1\ N\ \text{Na}_2\text{S}_2\text{O}_3$$

A modification of the permanganate test which finds some use in mill control is carried out by adding, to the well-washed pulp, permanganate solution insufficient to oxidize the impurities completely and noting the time required for the color to be discharged. The temperature and other conditions need very careful control if reliable results are to be obtained, and at that it is probably not so accurate as the methods just described.

Chlorine Consumption. In 1924 Roe[49] described a method and apparatus for determining the chlorine which an unbleached pulp would absorb under standard conditions and suggested that this might be translated into the bleach required. Since then this method and its

modifications have been widely used, both here and abroad. Johansson[18] defines the Roe chlorine number as the grams of gaseous chlorine absorbed in 15 minutes at 20° C. by 100 grams of dry pulp, which has been moistened until it contains water equivalent to 122 per cent of its dry weight. It ranges from 1.5 to 13 for ordinary sulfites and from 1.5 to 9 for sulfate pulps.
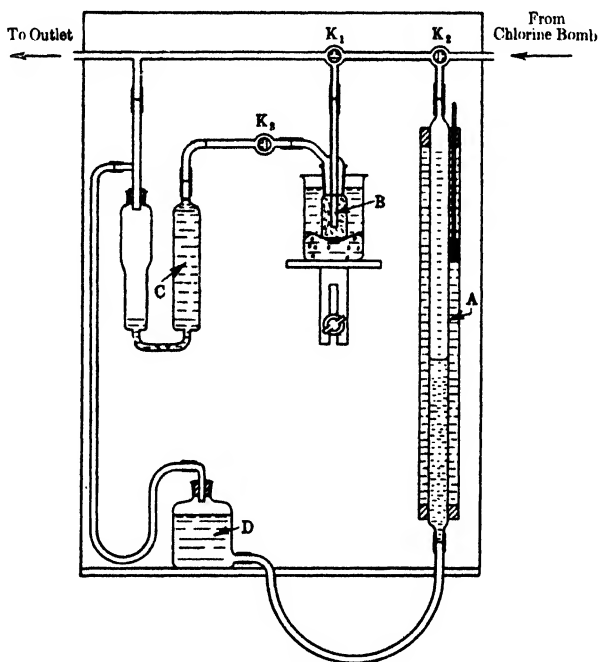
FIG. 49. MODIFIED ROE CHLORINATION APPARATUS.

Johannson's modification of Roe's apparatus is shown in Fig. 49. Burette A contains a solution of 30 grams of $CaCl_2$ in 100 grams of water; this is saturated with chlorine daily. This is also used in the vessel C, which is filled to a mark on the left arm. With an empty reaction bottle in place at B the liquid in C is sucked to the top of the right arm and cock $K3$ is closed. Burette A is then rinsed twice with chlorine, about 100 cc. of the gas taken in, and the volume measured accurately. The reaction bottle with the moist pulp at 20° C. is then placed in the water bath B, which is also at 20° C., and any pressure is released by opening cock $K1$ momentarily. Gas from A is then passed through $K2$ and $K1$ into B, while $K3$ is open to relieve pressure. Leveling bottle D is so manipulated that the liquid levels in A and D

are the same during the absorption period of 15 minutes, after which the liquid in C is again brought to its original level, cock $K3$ closed, and the volume of gas in A read at atmospheric pressure.

Since pure filter paper shows a chlorine absorption of 4 cc., this volume is to be subtracted from that absorbed by the sample. The chlorine number may then be calculated by the following formula:

$$\text{Chlorine No.} = \frac{0.0004168(V-4)h}{fg}$$

in which V = volume of chlorine gas absorbed in cubic centimeters.

h = barometric pressure in millimeters of mercury.

$f = 1 + 0.00367t$.

t = temperature of chlorine in degrees centigrade.

g = grams oven-dry pulp.

The chlorine consumption of pulp may also be measured when determining the cellulose,[62] and there are doubtless many other modified methods for accomplishing the same result.

Loss in Weight on Bleaching. In commercial bleaching there are two sources of loss — mechanical and chemical. Mechanical losses should naturally be kept as low as possible, but they are not in any sense a function of the pulp used. Chemical losses, on the contrary, vary considerably with the quality of the pulp and with the bleaching methods employed.

Chemical losses may be determined by bleaching a sample of known bone-dry weight with the amount of hypochlorite indicated by the bleach requirement test. After the bleach is exhausted the pulp must be washed very thoroughly with hot water, dried at 100°–105° C., and weighed. The difference between this weight and the original dry weight gives the loss due to the bleaching action.

Since the chemical loss on bleaching is usually not great it is generally sufficient to make the test as a single-stage bleach, but if a more accurate comparison with mill operations is desired it should be made to conform with the bleaching system used.

Nature and Amount of Dirt. The estimation of dirt is an important step in pulp evaluation, but methods entirely free from objectionable features have not been developed. The chief difficulty is to decide what constitutes dirt and how small particles to include in the count. No two persons will agree on this, and the same individual will vary from day to day and with the quality of the pulp being tested. There is always a tendency to be too severe on extra clean pulp and lenient on very dirty lots, thus making them appear more uniform than they actually are. The nature of the dirt and its color must be considered;

a large, black spot of a soft, friable nature may easily be less harmful, though more conspicuous, than smaller spots of hard, brown bark. The standards for cleanliness will vary with the service the pulp is to perform; one to be employed unbleached should be cleaner than one which is to be bleached before use.

A fairly satisfactory method for estimating dirt is to wet the pulp sheets and place them over a brightly illuminated background. The specks on the surface, as well as many in the interior, can be counted, and their nature investigated by means of a needle. If both sides are counted and the area known, a record is easily made of the count per 100 square inches, or if it is desired on the weight basis the pulp sheets may be weighed before wetting them. Classification of the particles into groups, such as shives, bark, cinders, and iron rust, often helps in locating the chief cause of the dirt.

A somewhat similar method[57] applied to relatively thin dry sheets counts the dirt in specified areas amounting to 5 square inches in each of four 5-by-5-inch sheets and uses a wide-field microscope tube fitted with a micrometer eyepiece having a magnification of 10 diameters. Each particle is measured on its longest dimension and classified into: small, between 0.5 and 0.15 mm.; and large, more than 0.5 mm. For shives the limits are between 1.0 and 0.15 mm. and larger than 1.0 mm. The results are calculated to the number of particles per pound of pulp.

Clark, von Hazmburg, and Knoll[11] use a chart containing black spots on a white background for comparison. These spots are arranged in groups of the same area in square millimeters, but are of different shapes, so that one resembling the speck under examination can usually be found. This method considers the dirt specks to be of the same area as the black spot on the chart which gives the same visual impression; a light gray spot would not be recorded as of its actual area but of the "equivalent black area." Specks of less than 0.03 sq. mm. are not considered. The samples are examined on one side only, while over a white background and illuminated from above, and the report gives the square millimeter of dirt per square meter of pulp.

This method would seem better for papers than for pulps since it is the visible surface dirt which is objectionable in paper. When pulp is used for paper making the dirt within the relatively thick sheet is released and made available for contaminating the paper, yet it is not considered in the testing method. For comparative purposes only, and where the thickness of the pulp sheet does not vary appreciably, the method seems to be the best at present available.

Chemical Properties. To the paper maker the chemical properties of pulps are of less interest than their physical tests, though there is often a close relationship. This has been brought out by McGregor,[31] who degraded pulps by acid, bleach, and heat to definite degrees of cuprammonium viscosity and found that viscosity changes were always accompanied by decided alterations in the physical and chemical properties, but that the correlation between these properties and the degrading influences depends on the type of pulp and the conditions of degradation. Unless the conditions of any work are stated the conclusions are of little value.

Alpha-Cellulose. One of the more important tests applied to pulps is that for alpha-cellulose, which is defined as that portion of the pulp which is insoluble in 17.5 per cent caustic soda solution under very carefully prescribed conditions.[64] Since the test is empirical the conditions must be followed exactly if duplication of results is expected. This method is time-consuming, and recently Launer[28] has brought out a volumetric method which is simpler and said to give essentially the same results.

In paper making, such tests are of value chiefly in indicating the probable stability of the pulp and its suitability for permanent papers.

Copper Number. The copper number of a pulp is the number of grams of metallic copper in the Cu_2O reduced from $CuSO_4$ by 100 grams of fiber.[65] It is considered chiefly as a measure of the oxycellulose in the pulp, but, as it is difficult to carry out and gives no information not given by the alkali solubility and the viscosity tests, it is seldom used.

Solubility in 1 Per Cent Caustic Soda. This test is particularly useful in determining whether the pulp has been degraded by too severe cooking or bleaching, especially the latter. The material dissolved includes pentosans and other carbohydrates which are less resistant than cellulose, as well as the cellulose which has partly broken down during its preparation. A satisfactory method[63] is to place a weighed sample of known moisture content in a 200-cc. tall-form beaker, add 100 cc. of a 1 per cent NaOH solution, stir until the pulp is completely disintegrated, cover the beaker with a watch glass, and place it in a steam bath or a steadily boiling water bath. Stir at the end of 10, 15, and 25 minutes, and at the end of the hour filter by suction on a tared crucible, wash briefly with hot water, then with 50 cc. of 10 per cent acetic acid, and finally with hot water. Dry, weigh, and calculate the loss on the oven-dry basis.

Ash. The ash in pulp may be determined as in paper, but on a considerably larger sample.[66] It has no significance in paper making but may be of interest in specialty or experimental pulps.

Cuprammonium Viscosity. This test requires special apparatus for preparing the cuprammonium solution, dissolving the pulp at 20° C., and testing the solution.[67] It is sensitive to changes in conditions and cannot be made without proper equipment.

The value of the test for paper-making fibers is somewhat questionable, and it is only when the viscosity of the pulp drops very low — usually less than 10 centipoises — that the quality of the paper suffers. The correlation between viscosity and paper qualities seems much closer in rag papers than in those from chemical pulps. Staudinger and Reinecke[58] concluded that viscosity tests showed little regarding paper-making properties. They found that in the high-viscosity region large viscosity changes might mean almost no change in paper strength, while at low viscosities great strength changes might accompany very slight ones in viscosity.

The test is of more value for pulps for chemical conversion, since it is supposed to measure the size of the micelle, which has an important bearing on the properties of the solutions and the regenerated cellulose. Micelle size is decreased by the chemical degradation of cooking and bleaching, and viscosity is the most sensitive test available to show such degradation. Reuben[47] concludes that the test must be used very cautiously in grading pulps of unknown history, but that it is useful in studying those from any one mill where treatments are relatively uniform.

Lignin. The usual method for determining lignin in pulps is to digest the sample with 72 per cent sulfuric acid for 16 hours at room temperature, then dilute to approximately 3 per cent acid concentration and boil for 2 hours to hydrolyze the cellulose and flocculate the lignin. Ritter, Seborg, and Mitchell[48] point out certain possible errors in this method and recommend first extracting the sample with alcohol-benzene and then with water, then digesting with 72 per cent acid for 2 hours at 20° C., and finally hydrolyzing the diluted mixture for 4 hours.

Noll's method[88] using sulfuric acid and dimethylaniline for digesting the pulp has been studied by Lewis, Koonce, and Young,[30] who found it to check the method employing 72 per cent acid fairly well on spruce pulps, but not on unbleached soda aspen pulp.

Pitch. The presence of pitch in pulp may be shown microscopically by staining with a strong solution of Sudan III[22] in a mixture of 3

parts of alcohol and 1 part of water, but as this alcohol concentration is capable of dissolving appreciable amounts of resin, some of the finer particles are likely to be lost.   In a more recent study of the Sudan colors Noll and Hahn[37] found Sudan Orange RR and Sudan Black B very satisfactory, while indophenol was also good.   Their stain may be made by mixing 3 volumes of 96 per cent alcohol with 1 volume of 31° Bé. glycerine and saturating this at room temperature with the dye.   Two volumes of this are mixed with 1 volume of glycerine of the same strength; the solution is filtered and is then ready for use.   It should be kept at 20° C. or higher to prevent precipitation of the dye. In use a sample of the wet pulp on a microscope slide is dried as much as possible by means of a filter paper, a drop of the stain added, and the cover glass put on.   It is usually found that most of the pitch in the pulp is present in the short fibers and ray cells.

For the quantitative determination of resin the method recommended by Launer[27] for paper may be followed, but the addition of acid to the alcohol is unnecessary.

It has been shown that all the resin in pulps is soluble in alcohol, but only part in ether.   As the latter seems more directly connected with pitch troubles it is desirable to extract the sample first with ether and then with alcohol, the two extracts being weighed separately.

Ragan and Kress[46] have shown that the usual extraction methods change the physical character of the pitch so much that studies of its properties are unreliable.   They propose the use of ethyl acetate under certain prescribed conditions and claim that the nature of the pitch is practically unchanged.   Though not strictly connected with the testing of pulps, reference should be made to a paper by Kress and Moss[25] which gives a survey of pitch troubles and a very good list of references.

Tests for Chemical Pulps.   Dissolving pulps, especially for viscose, must be highly purified and uniform in quality throughout any shipment, and from shipment to shipment.   Uniformity of viscosity of viscose made from successive lots is of primary importance; the viscosity is considered uniform if viscose made from 60-pound samples of successive lots of pulp does not vary more than 6 per cent from the average of 10 such lots.   If smaller samples are used somewhat wider variations may be expected.   It is not recommended that viscose be made from less than 1 pound of pulp.

The pulp should also show uniformly high solubility, which is measured by the filtration characteristics of viscose made from successive lots.   Further, the viscose must be free from undesignated impurities which adversely affect spinning in the plant.

In control in pulp mills, uniformity is judged by that of the cuprammonium viscosity of the pulp. This test is not appreciably affected by small amounts of iron, manganese, and other metals, which have a very great affect on viscose, so the final decision must rest on the xanthate viscosity. For a pulp having uniform foreign material there is usually a fairly constant relation between the two viscosities, but this relation does not hold for all pulps; a linter pulp, for example, and a wood pulp with the same xanthate viscosity will have radically different cuprammonium viscosities.

Uniformity is also judged by the alpha-cellulose content of the pulp, which should not vary more than ±1 per cent from the average. This test also gives some indication of the loss which may be expected during the alkaline treatment in viscose preparation.

Other tests which are of importance for dissolving pulps are of a chemical nature, and the methods in general use are those of the Forest Products Laboratory and T.A.P.P.I. It is not possible to describe in analytical terms a pulp which could be guaranteed suitable for viscose, but one with the following characteristics would be expected to make satisfactory rayon or Cellophane:

	PER CENT
Alpha-cellulose	88 or more
Beta-cellulose	4 or more
Ash	0.10 or less
Iron	0.0010 or less
Copper	0.0005 or less
Calcium	0.03 or less
Magnesium	0.005 or less
Silica	0.01 or less
Manganese	0.0001 or less
Solubility in 10% KOH	18.0 or less
Solubility in ether	0.6 or less
Copper number	1.75 or less
Lignin	0.2 or less

Interpretation of Pulp Tests. In a pulp mill the standards for quality are usually set by the use to which the pulp is put, and the tests applied are designed to show how nearly it reaches those standards, but above all how uniform it is. The paper mill wants to know also whether the pulp will make the grade of paper to be produced and how it should be treated to bring out the best there is in it. The correlation of laboratory tests and mill operations requires close cooperation and much experience, but if the tests are made and judged skilfully they may be of great help to the purchasing department and to the paper maker.

Since papers must have different properties for different purposes it seems logical to judge pulps by their individual strength tests, as burst, tear, fold, tensile, and shrinkage. This makes it possible to select a pulp giving the most of the strength factor desired, which cannot be done if the tests are combined by any formula into a " general strength factor." Such a combination may give an accurate picture of the average strength of the fiber and show when the treatment is causing deterioration, but it does not tell what factor is being most affected.

Of the individual strength factors burst and tensile strength usually go together, and of two papers of equal tensile strength, that with the least stretch will burst soonest. Stretch is a valuable indication of toughness and, when considered with the tensile strength, gives a better idea of quality than does burst alone.[8] The folding strength tends to follow in general the course of the bursting test, but to keep on rising after the latter starts to fall. Tear is to some extent a measure of fiber length plus cohesiveness. With most fibers there is a rise in tearing strength during the first part of a laboratory pebble mill beating, but this takes place so early, and the drop in tear follows so quickly, that the effect is often overlooked. Clark states that this initial rise in tear also takes place in mill beaters. He also calls attention to the desirability of considering the bulk or specific volume of the test sample because of the light which it throws on sheet properties when considered in conjunction with the other tests.

As an aid to pulp evaluation Rothchild[50] suggests the selection of a standard pulp which would be given a rating of 100; all other tests could then be based on this so that relative ratings would be numerical. This might be an excellent plan but for the fact that length of storage of pulp samples seriously alters their strength tests.

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CHAPTER XVI

PAPER TESTING

E. SUTERMEISTER

This chapter describes the methods in common use in testing paper, but not those which are applicable only to particular kinds of paper or to show its value for certain special uses. Such tests have relatively limited application, and their inclusion would make the chapter entirely too long. It has been attempted to present the methods concisely but in sufficient detail for any technically trained person to understand their principles. Intelligent interpretation of the results is as important as correct testing methods, but it can come only from experience, for which even the most minute details in methods are unsatisfactory substitutes.

The essentials of most of the methods have been taken from those adopted by the Technical Association of the Pulp and Paper Industry (T.A.P.P.I.), which should be consulted if further details are desired. Reference to these methods does not mean that all the facts given are contained in, or vouched for by, the standard method. Personal opinions and experience have been inserted wherever it was considered desirable.

The literature of paper testing is very voluminous and is excellently covered in C. J. West's " Bibliography of Paper Making."[43] The more pertinent references are also given in the T.A.P.P.I. methods cited, and some additional ones in a list at the end of the chapter.

Sampling.[16] Because of the variations in paper and because even adjacent sheets in a case may be from different machine runs, extreme care must be taken to obtain a representative sample for testing. When paper is shipped in cases, frames, or bundles at least 10 sheets not less than 11 by 11 inches should be taken and they should be drawn from not less than 2 nor more than 5 per cent of the total number of units in the shipment. From each unit sampled, 5 to 10 consecutive sheets should be taken at least $\frac{1}{2}$ inch from its surface. In the case of roll paper 1 or 2 sheets may be taken the full width of the roll from the first unharmed layers.

The sheets should be kept flat and smooth, should be handled as little as possible, and should be protected from exposure to strong light, laboratory fumes, etc. These precautions are especially necessary when tests for optical properties or acidity are to be made.

MICROSCOPIC TESTING

The microscope has many uses in paper making and is of particular value in determining its fiber composition and in tracing sources of defects such as specks and spots. An excellent bibliography on the subject as a whole has been prepared by Calkin.[41]

The microscope chosen should be of some standard make so that attachments may be added from time to time as seems desirable, but the particular kind, and whether monocular or binocular, is largely a matter of personal preference. This is true also of the magnification employed, some advocating 45 diameters and others as high as 160. An instrument with $\frac{2}{3}$- and $\frac{1}{4}$-inch objectives and 1- and 2-inch eyepieces will give as great a range of magnification as is necessary for all ordinary paper-mill work. A substage condenser and iris diaphragm should be included, and it is very desirable to add both a stage and an eyepiece micrometer.

The material to be examined is generally placed on a slide of thin, clear glass about 1 by 3 inches and covered with another slide or a very thin cover glass which flattens and protects the material and keeps any fluids in place. Needles are required for teasing out fragments of material, separating fibers, etc. Needles are made especially for this purpose, but a stout sewing needle with the eye end forced into a pine stick will serve equally well. The stains for fiber identification are best kept in amber-colored bottles fitted with ground-in dropping tubes and rubber bulbs.

Illumination is a very important feature in microscopy, particularly when viewing the colors of stained fibers. A clear north light is preferred, but good results can be obtained with an electric lamp having a blue " daylight " filter. The beginner generally uses too strong light and thus fails to observe details which are visible with lower illumination.

Fiber Composition.[17] Fibers are identified by their characteristic form and structure and by the colors they develop with various stains. Known mixtures of fibers must be used for reference when in doubt concerning determinations and for periodic testing of such stains as may change with age. An experienced analyst can usually estimate the fiber percentage within 5 per cent of the true value unless the mixture is very complex. The percentage is based on the total fiber content; e.g., if a paper contains no fiber other than rag it is reported as containing 100 per cent rag fiber, regardless of whether it contains filler or any other non-fiber materials.

To obtain representative samples several small pieces should be cut from various parts of the sheet, or from each of several sheets if

available.   These should be placed in any suitable container, covered with 0.5 per cent caustic soda solution, and heated to boiling, to dissolve sizing or binding materials.   The sample is then washed several times in water, rolled into a ball, kneaded between the thumb and finger, and finally reduced to a pulp by shaking vigorously in a test tube about half full of water.   A small sample is removed from the tube by means of a needle, placed on a microscope slide, and the water removed by touching the drop with a piece of folded filter paper.   The fibers are covered with the appropriate staining and mounting media, carefully separated by the aid of needles, so that they will not lie too much in bunches, and then a cover glass is put on.   The slide is then ready for examination.

In this work a number of precautions must be observed if good results are to be obtained, and a discussion of some of these points will be helpful, at least to those who are beginning the work.

There are several methods for removing representative samples from the test tube.   Spence and Krauss[14] prepare a dilute pulp in a test tube about $\frac{3}{4}$ by 8 inches and for removing the sample use a glass tube 10 inches long and 7/32 inch in diameter, fitted with a small rubber bulb at one end and with the walls at the other rounded to a smooth edge.   The test tube is well shaken, the dropper quickly inserted 2 inches below the surface, two bubbles of air expelled, and about $\frac{1}{2}$ inch of mixture drawn into the tube.   This entire portion is transferred to slides, making 4 drops in all, and the water is removed by evaporation in an air bath.   The slides are then ready to stain and examine.

Another method is to prepare the mixture in a smaller test tube and after shaking vigorously insert a microscope needle and take out a small bunch of the fibers.   This is better for long-fibered stock such as bond, ledger, and writing papers; the first method is safer for groundwood papers and others where very short fibers are present.

The second method may be made applicable to all grades of paper by preparing the mixture of such density that, on shaking and then placing the tube upright, small clots of fiber will remain adhering to its walls above the liquid.   The sample is then obtained by removing all the fiber in one of these small clots.

Removal of the water from the sample before staining may be done by evaporation, with a filter paper, or by pressing a blotting paper of firm texture directly on the drop on the slide, thus leaving the fiber adhering to the slide ready for staining.   If the blotter is free from lint, and any loose fibers are blown from its surface just before use, no contamination of the sample need be feared.

The stains most generally used are the Herzberg, the Lofton-Merritt, and the Bright (as modified by Kantrowitz and Simmons). These are prepared and used as follows.

Herzberg.[7]

> Solution A: an aqueous solution of C.P. zinc chloride (fused sticks in 50-gram sealed bottles) saturated at 20° C.
> Solution B: 0.25 gram of C.P. iodine and 5.25 grams of C.P. potassium iodide dissolved in 12.5 cc. of distilled water.

Prepare the two solutions separately, mix, and allow the mixture to stand several hours until all sediment has settled. Decant the clear liquid, which is then ready for use. This stain colors groundwood, jute, flax tow, unbleached manila hemp, and practically all highly lignified fibers yellow or lemon yellow. Thoroughly cooked and bleached soda and sulfite pulps as well as bleached straw and esparto fibers are colored blue or navy blue. Cotton and linen rags, thoroughly cooked and bleached manila hemp, and some of the Japanese fibers are colored wine red.

It is very essential that this stain be so made as to give satisfactory colors on the different fibers. Its quality should be proved by staining a mixture known to contain about equal proportions of rag, bleached sulfite, and bleached soda fibers. If the stain is satisfactory the soda pulp will stain a dark blue; the sulfite, because of its thinner walls, a light blue; and the rag fibers, red or wine-red. If the blue is not clear, but tends toward the violet, too much iodine is present and more water or zinc chloride should be added. A stain which gives the best results with groundwood will not always be entirely satisfactory with mixtures of well-bleached fibers, and if widely varying papers are to be examined it is well to keep on hand a number of stains so adjusted that one suitable for any grade of fiber is available.

Lofton-Merritt.[13] This stain is used to differentiate between unbleached sulphite and unbleached sulfate (kraft) fibers. It is prepared as follows:

> Solution A: 2 grams of malachite green in 100 cc. of water.
> Solution B: 1 gram of basic fuchsin in 100 cc. of water.

These are mixed in the proportions of 1 volume of A to 2 volumes of B. The compound stain is added to the fibers and allowed to remain 2 minutes, the excess is removed, and then a few drops of 0.1 per cent HCl are added. After about 30 seconds the excess of acid is removed, replaced with water, and again removed. Unbleached sulfate fibers are stained blue or blue-green, and unbleached sulfite fibers purple or lavender. If any purple fibers appear in unbleached

sulfate, too much fuchsin is present and more malachite green should be added to the mixed solutions. The appearance of green or blue fibers in unbleached sulfite shows the need for more fuchsin in the mixture.

Modified Bright Stain.[2] This stain is to distinguish between unbleached and bleached fibers. According to the modification of Kantrowitz and Simmons it is prepared and used as follows:

Solution A: 2.7 grams ferric chloride ($FeCl_3 \cdot 6H_2O$) per 100 cc. of distilled water.

Solution B: 3.29 grams potassium ferricyanide ($K_3Fe(CN)_6$) per 100 cc. of distilled water.

Solution C: 0.5 gram benzopurpurin 4B crude in 100 cc. of 50 per cent ethyl alcohol. The dye should be du Pont's purpurin 4B concentrated, or its equivalent. The solution should be warmed until it is completely dissolved, but some of it will precipitate on cooling.

Filter solutions A and B and keep in separate bottles; these solutions need to be renewed frequently. Solution C will keep indefinitely; whenever it becomes cloudy it should be warmed until clear. In using this stain apply 3 drops of each solution, A and B, to the fibers, allow to stand 1 minute, remove the excess, add a few drops of solution C, allow to stand 2 minutes, and again remove excess fluid. Bleached fibers or those practically free from lignocellulose are colored red; unbleached fibers or those containing appreciable amounts of lignocellulose are colored blue.

Graff[4] claims that the Bright stain does not properly distinguish between bleached and unbleached fibers, but that it is a quick method for determining the degree of cooking and uniformity of a pulp.

Modified Iodine Stains. The following iodine stains are also useful in fiber analysis, but whether they are superior to the Herzberg stain is largely a matter of personal opinion.

The Sutermeister stain uses the following solutions:

A: 1.3 grams iodine and 1.8 grams KI in 100 cc. of water.
B: a clear, practically saturated solution of $CaCl_2$.

In using this stain apply a drop or two of solution A to the moist fibers on the microscope slide. After a minute or so remove the stain by a blotter and immediately put on a drop of solution B. Pull the fibers apart, distribute them by means of needles, and drop on a cover glass. Any excess of solution should be removed by a moist blotter. This stain is selective in action and gives the following colors:

Red or brownish red: cotton, linen, hemp, and ramie.
Dark blue: bleached soda pulps from deciduous woods.

Bluish or reddish violet: bleached sulfite fibers and the thoroughly cooked part of unbleached sulfite.

Greenish: jute, manila, and the more lignified fibers in unbleached sulfite.

Yellow: groundwood.

One of the advantages of this stain is the permanence of the solutions; light does not injure them, and they need be protected only from dust and evaporation.

The Selleger stain is particularly useful for papers containing soda pulp, esparto, or straw. A modified stain, which will retain its strength for 2 or 3 months, may be made by dissolving 100 grams of $Ca(NO_3)_2$ in 50 cc. of water, adding 3 cc. of a solution made by dissolving 8 grams of KI in 90 cc. of water, and finally adding 1 gram of iodine. After standing for a week the solution is ready to use. The colors it gives are as follows:

Light rose: bleached coniferous wood.

Clear yellow: unbleached coniferous wood.

Violet blue: poplar, birch, and straw.

Wine red: manila and hemp.

Rose-brownish: linen and cotton.

Deep yellow: groundwood, jute, and uncooked straw.

The Graff "C" stain[5] is helpful to the expert in making unusual distinctions among different types of chemical wood pulps, including the highly purified fibers. This stain contains iodine with $AlCl_3$, $CaCl_2$, and $ZnCl_2$, which must be dissolved to exact strengths and combined in very definite proportions. Special care and experience are required for its successful use, and, as slight color differences are significant, authentic reference samples of pulps and papers are needed for comparison, and the colors should be referred to Ridgway's Color Charts or their equivalent. The microscopic technique is more exacting than for most fiber analyses, and the method is not one which should be used by the inexperienced.

The percentages of the various kinds of fibers in paper can be determined by the count or the estimation method. In the count method the fibers of each kind are counted and the proportions of each calculated by means of weight factors which compensate for the relative weights of equal lengths of the different kinds of fibers.[14] In the estimation method the unknown sample is compared with standard samples of known composition. This method requires considerable experience and frequent reference to the standards, but it is quicker than the count method and no weight factors are needed.

In using the count method, which has been adopted as the standard

procedure by T.A.P.P.I., a reference point in the eyepiece of the microscope is required. A cross-line disk to fit into the eyepiece can be purchased, or the reference point can be made in the laboratory in various ways. In use the slide is moved so that five trips across the field are made about 5 mm. apart and each fiber passing under the reference point is counted as one regardless of its size. The distribution of fibers should be such that about 200 to 300 are counted, and in aggregations of fibers the number of single fibers in the aggregation is estimated. The number of each kind of fiber is multiplied by its weight factor to obtain a weighted count. The factors most generally accepted are: groundwood, 1.3; rag, 1.0; chemical coniferous wood, 0.9; and chemical deciduous wood, 0.6.

Spot Stains. Though not a part of microscopic testing, spot stains are mentioned at this point because they are used to identify groundwood fibers. The stains are dropped on the paper to be tested and any development of color noted. To be indicative the color must be distinct; any slight discoloration should be disregarded.

Phloroglucinol solution, containing 5 grams of phloroglucinol in 125 cc. of water and 125 cc. of concentrated hydrochloric acid, is the stain most generally used, though its strong acidity makes it somewhat objectionable. It gives a magenta color with groundwood, but only a slight yellowish color if it is absent.

Paranitroaniline, 1 gram dissolved in 405 cc. of water and 30.5 cc. of sulfuric acid (sp. gr. 1.84), gives an orange yellow with groundwood. As the acid is not volatile it does not cause corrosion of adjacent metallic objects, and the stain does not deteriorate as rapidly as phloroglucinol.

Aniline sulfate as a saturated solution acidulated with 1 drop of sulfuric acid for each 50 cc. gives a yellow color. This does not have quite the sensitivity and color contrast of the other stains.

These stains are used to a considerable extent in sorting waste papers for the manufacture of paper which must be free from groundwood.

The phloroglucinol method was at one time worked into a quantitative method for groundwood[3] but it is probably never used for that purpose now.

IDENTIFICATION OF SPECKS AND SPOTS

Visible imperfections in paper are particularly objectionable and often cause an appreciable lowering of its value, or even its rejection by the customer. It is important to the paper maker, therefore, that the source of defects be located as quickly as possible, and proper cor-

rective measures taken. Following are some of the more common types of imperfections and suggestions as to their identification.

Alum spots are soluble in water and give a slightly acid reaction with indicators.

Bark spots are usually readily disintegrated into brown particles.

Bleach scale consists of pearly, light brown, brittle particles which effervesce when treated with dilute hydrochloric acid.

Bronze specks have a shiny, metallic appearance and give a red coloration when treated with hydrochloric acid and potassium ferrocyanide.

Button specks resemble alum spots, but are hard, insoluble in water, and give no color reaction with indicators.

Coal specks are insoluble and give no color reaction with any reagent. Large particles give a characteristic black smear when crushed and rubbed across the sheet.

Cinders usually resemble coal specks but are frequently harder and may give a reddish brown smear instead of a black one.

Color specks can usually be told by their relatively soft texture and characteristic color.

Iron specks, if in metallic form, are attracted by a magnet. These, as well as oxidized iron, except Fe_3O_4, give a blue color when treated with hydrochloric acid followed by potassium ferrocyanide solution.

Resin specks may come from wood pulp or from rosin size. They are usually translucent, amber-colored, and soft, and are often soluble in ether. When touched with a hot needle they give a characteristic odor.

Rubber particles generally come from waste paper stock or rags. They swell in benzene, dissolve in carbon tetrachloride, and give a characteristic odor when burned.

Paper and fiber lumps may originate from undefibered paper, knotted threads of rag stock, or lumps of stock from the wet end of the paper machine. They can often be identified by their fibrous nature, but their presence may be overlooked because they are often crushed to transparent spots by the calenders. In such cases soaking in water will often cause them to regain their original opacity.

Foam spots are usually circular spots which are more translucent than the rest of the sheet.

Oil spots may frequently be detected by the " halo " extending outward from the main spot. They dissolve in great part in oil solvents and, in common with resin spots, they may be stained by means of Sudan III.

Slime spots are caused by growths of bacteria or algae combined with fibers; the lumps break away from the wet end of the machine,

do not dry sufficiently in passing the dryers, and are crushed by the calenders into irregular, translucent areas. They often cause holes in the sheet.

Wood particles or "shives" may come from wood pulp or from wooden equipment. Their fibrous nature is usually evident, and sometimes they will give the characteristic color with phloroglucinol, though not when they originate from an old jordan filling or come from recovered paper stock which has been cooked with alkali during recovery.

PHYSICAL TESTING

The physical testing of papers and paperboards is very complex because of the great diversity of use requirements as related to physical properties. Weight and thickness; extensibility with change in moisture content or under applied stress; permeability to various liquids and gases; strength and other mechanical properties; and the properties related to appearance, such as finish, formation, color, and opacity — are all of importance and their determination requires a wide variety of testing instruments. Only the more common types are mentioned in this section, though there are others which are as good or better for certain purposes. The successful use of instruments depends on their potential accuracy and on the care taken in their use, maintenance, and calibration. For some instruments permanent reference standards are available for checking the accuracy of their performance; in their absence it is sometimes desirable to compare the performance of one instrument with that of another. References to existing standards and detailed instructions for the care of the standard testing instruments are contained in the T.A.P.P.I. methods.

Conditioning.[18] Since the physical properties of paper change with variations in its moisture content, it is necessary to condition it at a definite and constant temperature and humidity if standard test data are to be obtained. This is done by exposing the paper to the standard conditions until its moisture content is in equilibrium with that of the atmosphere, and then testing in that atmosphere. Formerly the T.A.P.P.I. standard conditions were 65 per cent relative humidity and 70° F., but in 1941 they were changed to 50 per cent relative humidity and 73° F., with tolerances of plus or minus 2 per cent and 3.5° F., respectively.

The time required for conditioning depends on the kind of paper under test and the degree of exposure, and varies from a few hours up to a day or more. For precise work the paper should be conditioned until it reaches practically constant weight, and for the most exacting
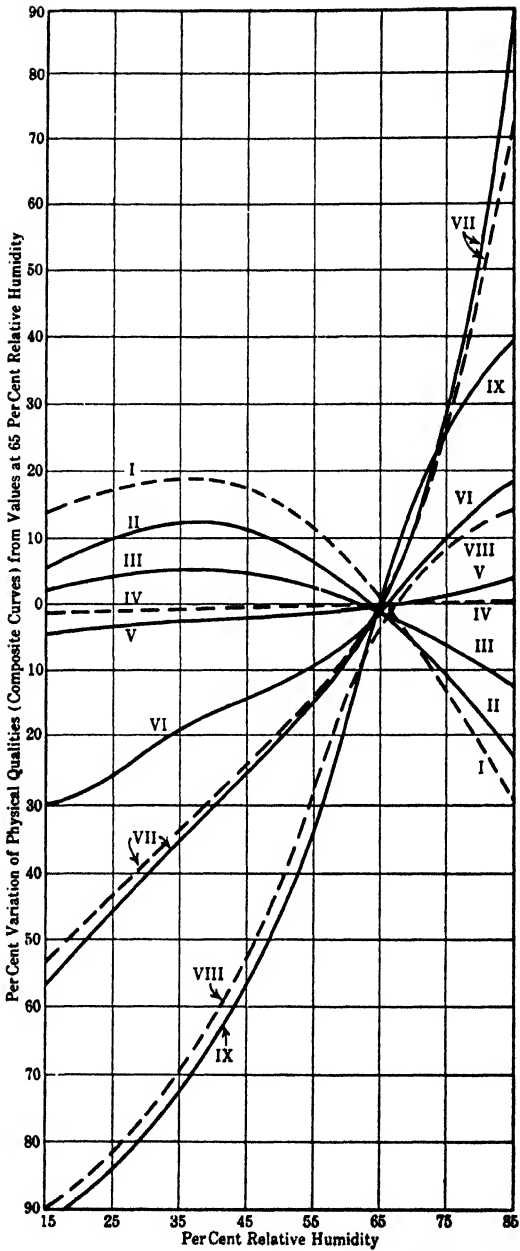
Courtesy Bureau of Standards

FIG. 50. EFFECT OF HUMIDITY ON PHYSICAL TESTS OF PAPER.

work it may be necessary to take into account the hysteresis in the equilibrium moisture content and condition all samples from the drier (or the wetter) state.

The effect of relative humidity on some of the physical tests of paper is shown in Fig. 50.[8]   In this figure curves I and II are for tensile strength, cross grained and with grain, respectively; curve III is for bursting strength; IV shows expansion and contraction; V is for moisture content, ream weight, and thickness; VI is for tearing strength; VII shows elongation under tension; and VIII and IX are for folding strength. From this it is evident that tests made under conditions without humidity control are of value only for comparison with those made at the same time; they cannot be used with safety to check papers against specifications.

Machine Direction.[19]   The tendency of the fibers to lie in the direction of travel of the paper machine usually causes the mechanical properties of paper to be different in the machine and cross directions. This makes it necessary to distinguish between the two directions when making and interpreting the physical tests; several methods are available.
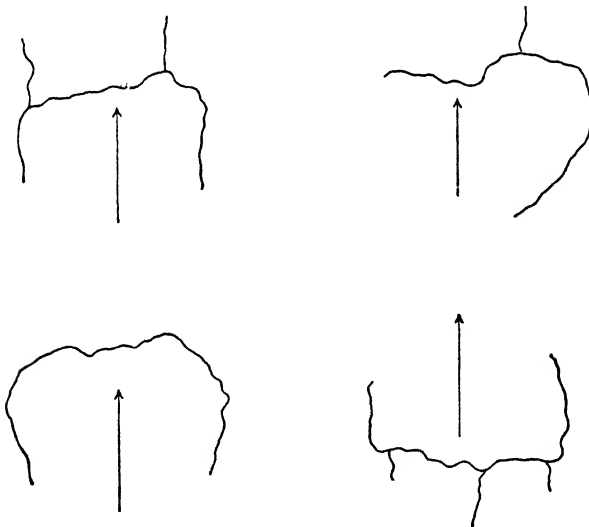
FIG. 51.   LINES OF RUPTURE IN MULLEN TEST.

If the mark left in the paper by the usual machine wire is sufficiently prominent to be visible it will indicate the machine direction because the long diagonal of the diamond-shaped marks coincides with the machine direction. Modern wires and paper machines often make

the wire marks so indistinct that this test cannot be applied with certainty.

If the paper is well sized and a circular piece is cut out and moistened on one side it will tend to roll up into a cylinder whose axis is in the machine direction of the sheet. Unsized paper will not show this test unless it is first sized with an alcoholic solution of rosin, or an aqueous gelatine solution, and dried before testing.

Another method of determining the machine direction is to cut two narrow strips of the paper, one from either direction, place these over one another, and hold them upright in the fingers. They will droop over of their own weight, and if they cling closely together the under strip is in the machine direction, but if the under strip falls away from the upper the latter is in the machine direction.

The form of the break made by the Mullen tester shows the machine direction, as the longest or chief line of rupture is always across the sheet. This is shown in Fig. 51, which illustrates four typical ruptures and in which the arrows indicate the machine direction.

Wire or Felt Side. A simple inspection will often show this, but in some papers the wire marks do not stand out at all plainly. Sometimes they may be made more prominent by plunging the sample for a moment into water and draining off the excess. The moisture thus undoes the work of the calenders and restores the texture of the sheet as it left the machine wire. This method often proves satisfactory, even for coated papers.

Basis Weight.[20] By this term is meant the weight of a ream of paper of a given size and number of sheets. Custom has established the ream sizes for different grades of paper as follows:

KIND OF PAPER	TRADE SIZE	SHEETS PER REAM
Writing and printing....................	17 × 22	500
Blotting..............................	19 × 24	500
Cover................................	20 × 26	500
Tissue...............................	24 × 36	480
Cardboard............................	22 × 28	...
Bristol and tag........................	22½ × 28½	500
News and wrapping....................	24 × 36	480
Book.................................	25 × 38	500
(T.A.P.P.I. standard size)..............	25 × 40	500

The term " substance number " is often used in expressing the ream weight of writing paper.

The basis weight is determined by weighing one or more sheets cut to a certain size, on scales or balances which are graduated to indicate the ream weight. The beam and quadrant types are commonly used

in the mill, but more accurate types are desirable for laboratory use.

If only a very small sample is available it may be weighed on a chemical balance and the basis weight calculated by the following formula:

$$\frac{(\text{Weight in grams}) \times (1.102) \times (\text{Area of trade size desired})}{\text{Area of sample in square inches}} =$$

Weight in pounds on trade size desired
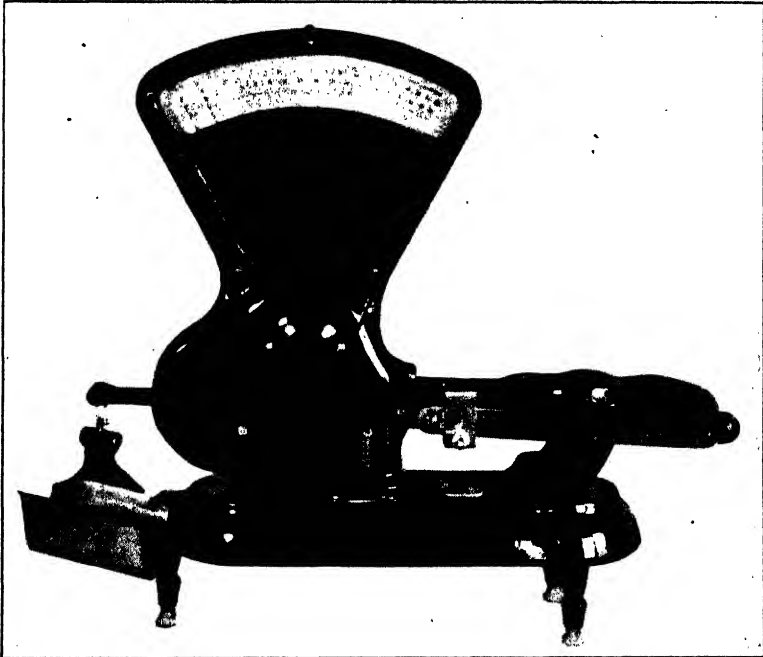
Courtesy of Toledo Scale Company

FIG. 52. REAM WEIGHT SCALES.

Thickness.[21] The thickness of paper is usually measured with a micrometer in which a single sheet is held under a given pressure between two circular plane, parallel surfaces, while the mechanism of the micrometer indicates the distance between them. The pressure applied is 7 to 9 pounds per square inch, and the smaller of the surfaces has an area of approximately 0.25 square inch. The dial micrometer is the common type, although a machinist's micrometer is sometimes used, particularly in the mill.

Bulking thickness is defined by T.A.P.P.I. as the average thickness

of a single sheet when a pile of several sheets is placed under a steady pressure of 7 to 9 pounds per square inch. The same dial micrometer serves as for single-sheet measurements. For mill control, where the number of pages per inch in thickness has to be regulated, a " pressure bulker " is more useful as it measures a larger number of sheets and the pressure applied can be regulated to suit the specifications of the publisher.

Expansion and Contraction. The change in dimensions of various paper products with change in moisture content often presents very serious problems. For example, misregister in multicolor printing may be caused, charts and maps may be thrown out of scale, and wall boards may buckle. The extent of expansion and contraction may be found by measuring the difference in

Courtesy E. J. Cady & Company

FIG. 53. THICKNESS GAGE.

dimensions on conditioning at different relative humidities. Special steel scales designed for high precision are available for such work, and there are also devices in which the changes in dimensions cause a pointer to move over a graduated scale.[6]

Opacity.[22] The opacity of paper may be measured in a number of ways. The most commonly accepted method gives values in terms of contrast ratio, which is the ratio of the reflectance of paper backed by a white background to that when backed by a black background. The reflectance when the paper is over a black surface is that from the surface of the paper only, as the transmitted light is absorbed, while the white background reflects the transmitted light also. The ratio is expressed as a percentage, being 100 for perfectly opaque and zero for perfectly transparent paper.

One method of measuring opacity is by a photometer containing a divided field which receives light reflected from the two areas backed by the black and white surfaces. The two halves of the illuminated field are matched by rotating a Nicol prism, and from the angular displacement, which is read on a scale, the opacity is calculated. A preferable type of instrument indicates the percentage opacity directly by means of a photoelectric cell. Opacity may also be determined with an instrument in which a microammeter and a photoelectric cell at a
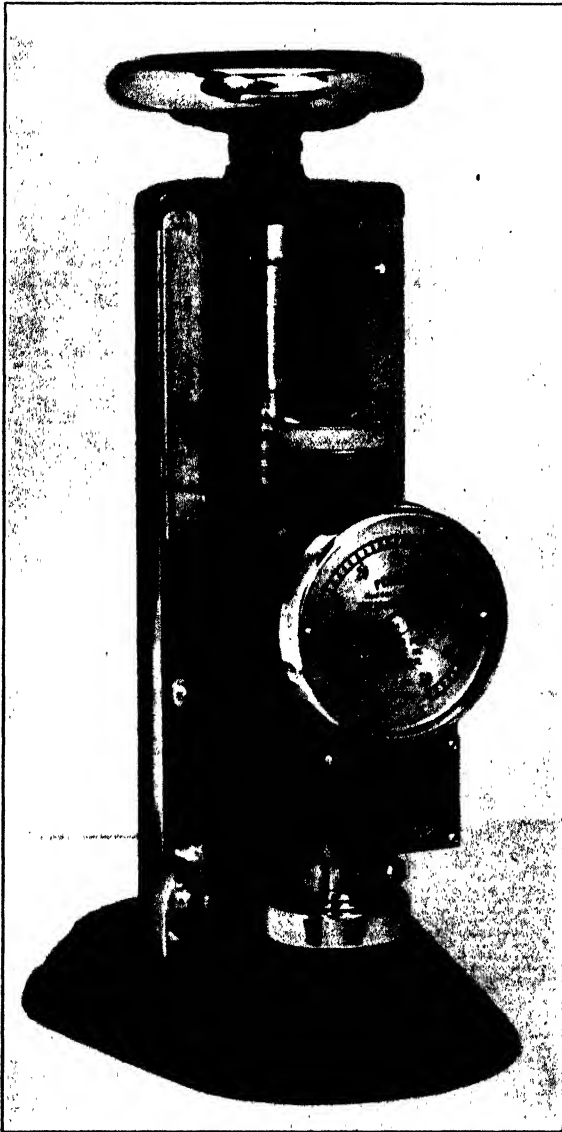
Courtesy of B. F. Perkins & Sons

FIG. 54.   PRESSURE BULKER.

fixed distance from a light source measure the transmission through the
paper when placed in the path of the light.
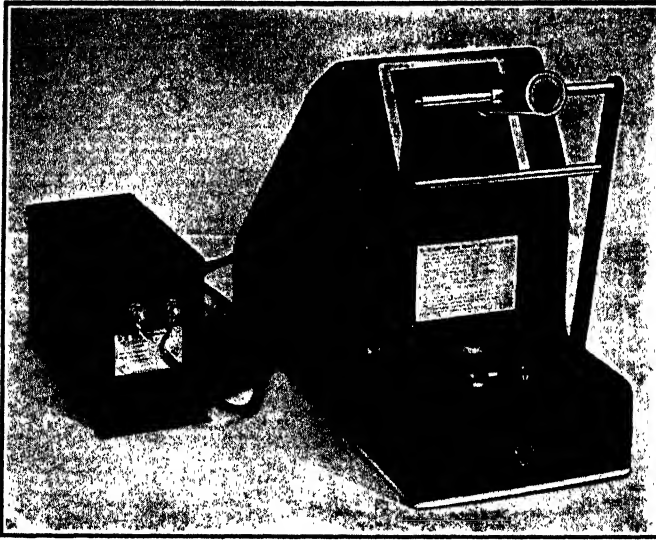
Courtesy Bausch & Lomb Optical Co.

FIG. 55.   BAUSCH & LOMB OPACIMETER
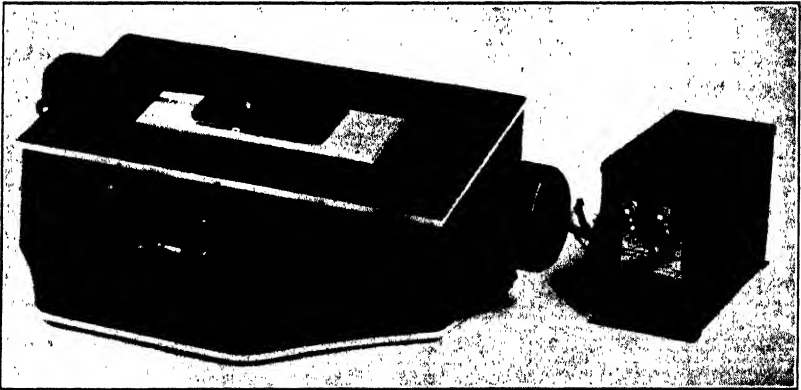
Courtesy of Bausch & Lomb Optical Co.

FIG. 56.   GLOSSMETER.

Gloss.[23]   The gloss of paper appears to depend upon the continuity
of its surface as well as on its planeness; a rough surface may still be
glossy, though the measurement of its gloss would be very difficult.

Gloss may be measured by the Ingersoll Glarimeter, in which a photometer is placed in the path of the reflected light to measure the fractional part which has been polarized. The angle of incidence is 32.5° with the paper surface, and readings are made by matching the halves of a divided field. These results are comparable only when papers of the same color are considered.

The Bausch and Lomb glossmeter, Fig 56, uses a photoelectric cell to measure the amount of light reflected at an angle of 15° with the paper and gives readings directly as percentage of gloss. This instrument is not affected by the color of the paper, and its readings check those obtained by visual grading of the same samples. Because of the difference in the theory on which these two instruments are based their readings may or may not check each other on the same samples; there is no fixed factor which will convert the readings of one to the other in all cases.

Color. In the estimation or measurement of color of paper a number of variables, such as surface texture, degree of opacity, and the kind of light in which the paper is viewed, must be considered. Many types of instruments are used for this purpose. Some measure photometrically the relative brightness of light of different colors reflected from the paper. Three colors, red, green, and blue, are sometimes used to represent the color characteristics over the spectrum. Another method is to match the color of the paper with a mixture of light of these colors, or with a mixture of white light with light of the dominant color of the paper.

Permeability. The permeability of paper products to liquids and gases is one of their most important properties as it affects nearly all their uses. Of particular importance is the permeability to liquid water, water vapor, air, inks, and grease or oil. Its determination is complicated by the wide variety of instruments and procedures which have been developed to show the suitability of the numerous grades of paper.

The resistance to penetration of aqueous fluids is often termed the " sizing " of the paper, and the test most frequently applied is to float the paper on writing ink at some definite temperature and note the time for the color of the ink to appear on the upper surface of the paper. Since the dye used in the ink may be selectively adsorbed by fiber or filler and its passage through the sheet thus greatly retarded, this test may bear no definite relation to the permeability of the paper to water. The personal factor in estimating the end point is large and has never been entirely removed by any of the modifications of the test which have been applied. This method of testing should be used for only the

roughest work, but if it is to be applied an ink of the following composition is recommended:

	GRAMS
Tannic acid	23.4
Gallic acid	7.7
Ferrous sulfate (crystals)	30.0
Dilute hydrochloric acid (10 per cent solution)	25.0
Phenol	1.0
Blue dye (Soluble Blue A)	3.5
Water to make 1000 cc. at 20° C.	

In preparing this, dissolve the ferrous sulfate in cold water, add the hydrochloric acid, and then the tannic and gallic acids dissolved in warm water. Finally add the dye dissolved in warm water, then the phenol, and make up to 1000 cc.

Permeability to water may be determined by the dry-indicator method[24] if the product under test is not in the absorptive class or is not too thick to make the test impractical. In this method the paper is sprinkled with a mixture of powdered sugar, dye, and starch and is then floated on water at some definite temperature, preferably 21° C. The time is taken from the moment the paper touches the water to the appearance of color in the indicator. Several methods have been devised for sealing the sample to prevent evaporation from its surface or the incorrect results due to the presence of saturated air around the indicator. If the paper is merely floated on water and the whole covered with a watch glass, the indicator absorbs moisture and the color develops before the water has actually penetrated the paper. The use of powdered potassium permanganate in place of the dry indicator is suggested as more accurate for this type of operation.

Water permeability may also be shown by the "curl test," which depends on the curling of the paper when it is wet on one side. The time required for the paper to curl to its maximum and start to uncurl is assumed to be one-half the time necessary for water to penetrate the sheet completely.

Another water-permeability test is that of Cobb[25] in which water is allowed in contact with a fixed area of paper for a definite time and the amount absorbed determined by the gain in weight of the sample. The method is suitable for paper and paper board 0.004 inch and over in thickness and is especially valuable in measuring surface absorption as distinct from total penetration.

In testing bibulous papers, such as toweling and blottings, a drop of water or a definite volume of ink is flowed onto the paper from a pipette and the time noted when light reflection from the wet surface ceases.[26]

Some idea of the resistance of paper to the penetration of oil can be obtained by applying castor or boiled linseed oil. If the paper is soft, a drop of oil may be applied directly; but if it is hard the oil should be spread out in a thin film by running a roller over it. Both these tests apply far more oil than would be present in a film of printing ink, hence any conclusions are of somewhat doubtful value if they are applied to printing problems.

A useful comparative test for grease resistance is to place lard or other fatty material between the specimens, lay a piece of white paper over each, hold the assembly together with light pressure, and note which paper first allows the fat to stain the white paper. The time of penetration of turpentine is also generally considered indicative of grease resistance. The turpentine may be confined on the paper by saturating a small pile of sand with it, and its penetration to the lower surface of the paper may be observed by means of an inclined mirror.

The permeability of paper to water vapor bears no relation to that of liquid water. Water-vapor permeability is commonly determined by fastening the paper over the mouth of a light vessel containing some drying agent, as magnesium perchlorate, and weighing the assembly at intervals after exposure to an atmosphere of high humidity.

The air permeability of paper may be determined by three classes of instruments, which: (1) compress the air and force it through the paper by hydrostatic pressure; (2) draw air through the paper by a partial vacuum; and (3) measure the pressure drop through the instrument caused by the resistance of the paper to passage of air. The first class is represented by the Gurley densometer (Fig. 57), the second by the Schopper densometer, and the third by the Emanueli porosimeter. Unless the paper is very permeable to air, leakage must be carefully guarded against, particularly around the clamp which holds the sample or through the edges of the specimen.

Smoothness. The "printing smoothness" of a sheet of paper is generally assumed to be correlated with, and measured by, the rate of flow of air between the paper and a plate pressed on its surface. This test appears to indicate fairly well the printing characteristics of news and similar papers of relatively coarse surface, but when applied to supercalendered or coated papers there is still some doubt as to its value.

Picking. The resistance of paper to picking, i.e., the flaking off of small particles from its surface, is of particular importance in printing, since picking may cause poor prints and necessitate cleaning up the press frequently. Coated papers may pick because of insufficient
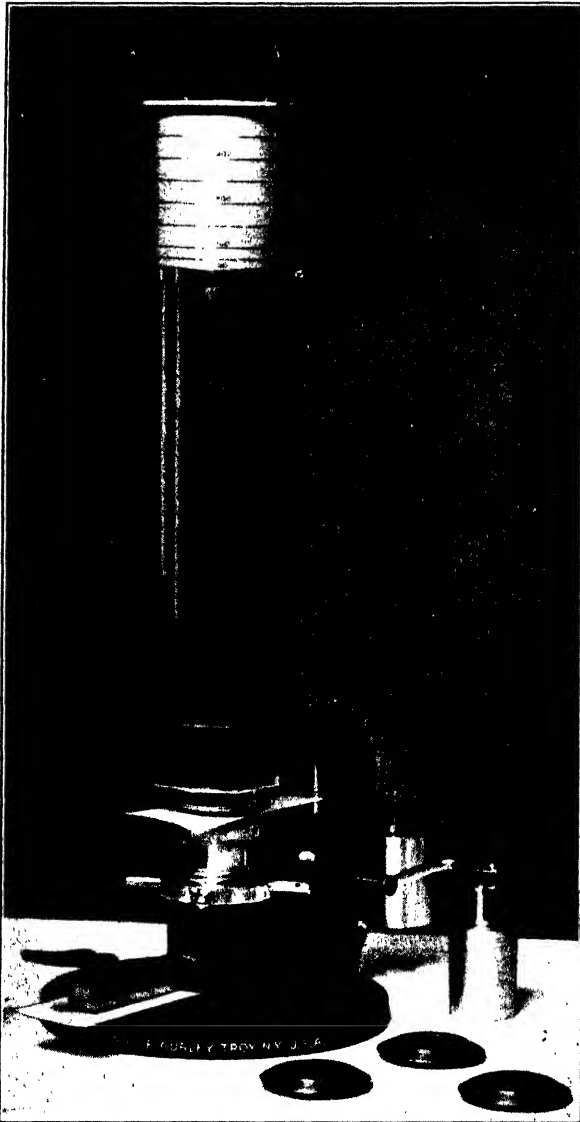
Courtesy W. and L. E. Gurley

FIG. 57.   GURLEY-HILL SOFTNESS-POROSITY-SMOOTHNESS TESTER.

adhesive or undispersed lumps of mineral matter in the coating; uncoated papers may pick because of fuzziness, dry froth, calender scale, or other material on the surface of the sheet, or because of internal weakness in the structure of the sheet. In the last case it may be bad enough to cause splitting or peeling.
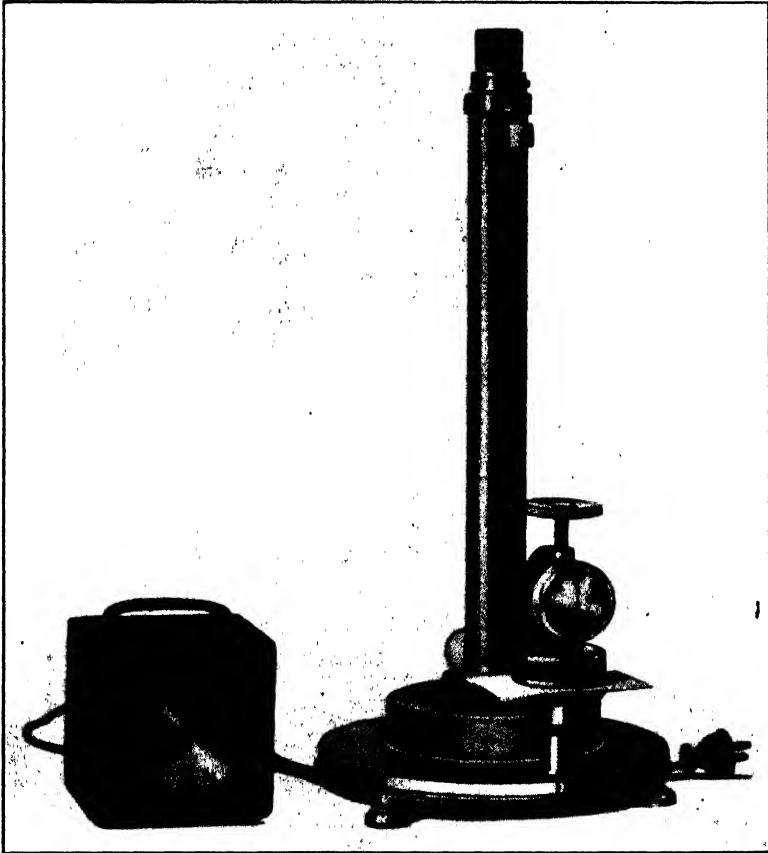
FIG. 58.   SMOOTHNESS TESTER.

There is no entirely satisfactory means of testing paper for picking. For coated papers a series of sealing waxes or graded adhesiveness is used with reasonable success for certain types of work. The conditions influencing their indications have not yet had sufficient study, and while they may be reliable for control work they are not satisfactory for research problems. When using these waxes the end of each stick is melted, pressed onto the paper to be tested, cooled, and pulled

off. The surfaces of the paper and wax are then examined to find which of the waxes first caused a rupture of the paper surface.

Paper may also be tested by actual printing, either on a commercial press or one designed especially for small samples. Numerous such
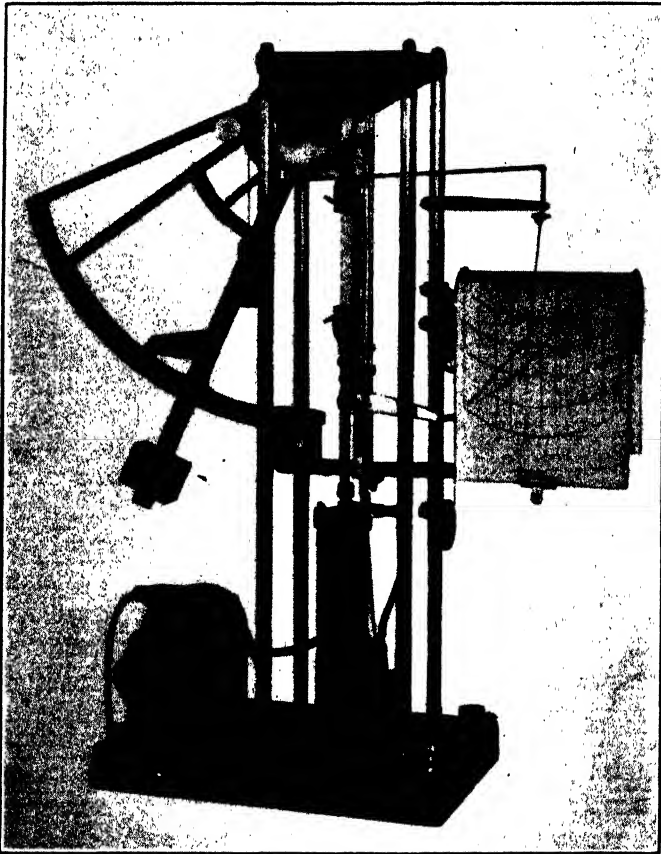
Courtesy Thwing-Albert Instrument Co.

FIG. 59. ELECTRO-HYDRAULIC TENSILE TESTER.

presses have been designed locally and give good comparative figures, especially when the unknown and a sheet of standard quality are printed side by side in one operation.

Strength. The tests commonly applied to show the strength of paper products are those for tensile strength, bursting strength, folding endurance, resistance to tearing, and flexural strength.

The tensile breaking strength of paper[27] is the load required to pull a strip of it apart. It is usually expressed as the kilograms required

for a strip 15 mm. wide, but the results may be converted to pounds per inch of width by the following formula:

(3.73) × (Tensile strength in kilograms per 15-mm. width) =

Tensile strength in pounds per 1-inch width

Tensile strength is often expressed as the " breaking length," which is the length of a strip of the paper which, if suspended at one end, would break of its own weight. This may be calculated by the following formula:

$$\frac{(\text{Tensile strength per 1-inch width}) \times (13,889)}{(\text{Weight of a ream } 25 \times 40 - 500)} =$$

Breaking length in yards

There are a number of instruments for determining the tensile breaking strength, all of which fasten the paper at each end in a clamp and cause the clamps to move apart until the strip breaks. The amount of elongation at the instant of rupture is also measured at the same time, the reading giving it directly as a percentage of the original length between the clamps.

Bursting Strength.[28] In making this test the paper is usually clamped beneath a metal ring which holds it firmly while pressure is applied underneath until it bursts. In one type of tester hydraulic pressure is used, while another employs air pressure. The maximum pressure required to burst the paper is indicated on a gage which registers in pounds per square inch, but the value is often expressed as " points." In another type of instrument, such as the Ashcroft tester, the force is applied by means of a metal plunger which is forced upward through the paper.

To be of the greatest value the bursting strength should take into consideration the weight of the sample tested. This will enable direct comparisons to be made of samples of very different thickness and weight. The ratio of strength to weight may be expressed as a percentage by the following formula:

$$\text{Bursting ratio} = \frac{\text{Bursting strength} \times 100}{\text{Weight in pounds (on a size } 25 \times 40 - 500)}$$

Folding Endurance.[29] This test is considered the best measure of the wear resistance of paper that is to be handled considerably, such as correspondence or record paper. The two types of instruments in common use for determining folding endurance are the Schopper and the M.I.T. testers. Both clamp a strip of paper under tension between

two sets of jaws and fold it back and forth until it breaks, the number of folds being indicated on a counter. The tension with the M.I.T. folder is constant throughout the fold, but can be varied at will to accommodate weak and strong papers; that in the Schopper folder varies from a maximum of 1000 grams to a minimum of about 730 grams during each individual fold.
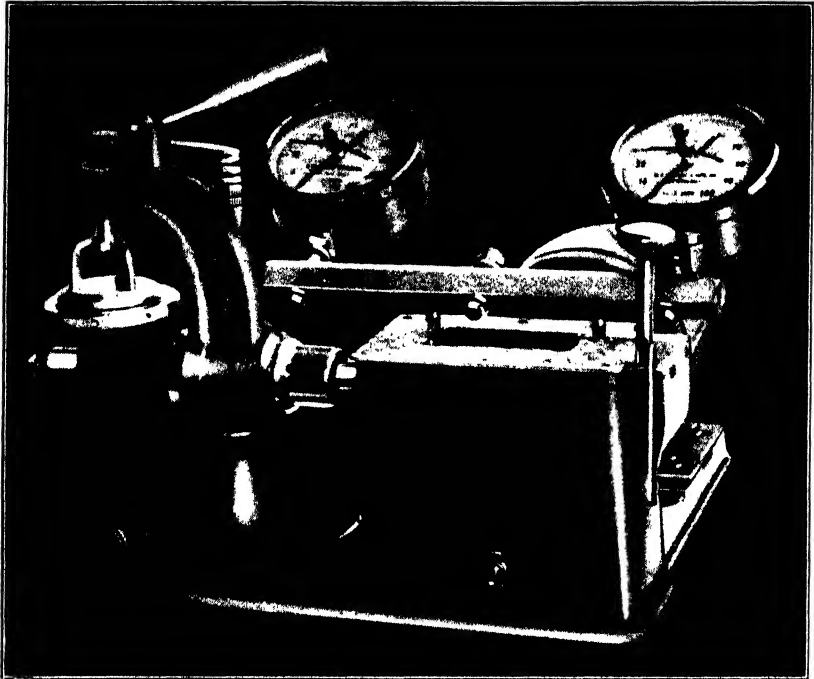
Fig. 60.   Mullen Bursting Tester.

. Of these instruments the M.I.T. is more easily checked and adjusted for accuracy, but the Schopper (Fig. 61) is the older and more generally used. Unfortunately there is no constant factor which will permit the reading of one instrument to be converted to that of the other.

The folding endurance of a paper varies more than most of its other physical tests, so, to obtain a fair average, not less than 10 strips should be tested, and with some papers even this is not enough.

Tearing Test.[30] The Elmendorf tester (Fig. 62) is the instrument in most general use for determining the tearing strength of paper. It consists of a pendulum carrying a movable jaw, which, initially is in line with a fixed jaw. The paper is clamped in the two jaws and a slit made by means of a knife attached to the instrument. The pen-

dulim is then released and in its swing tears the paper. A pointer indicates on a scale the force required.

The instrument is designed to show the force in grams when 16 sheets are torn simultaneously; if fewer sheets are torn the reading
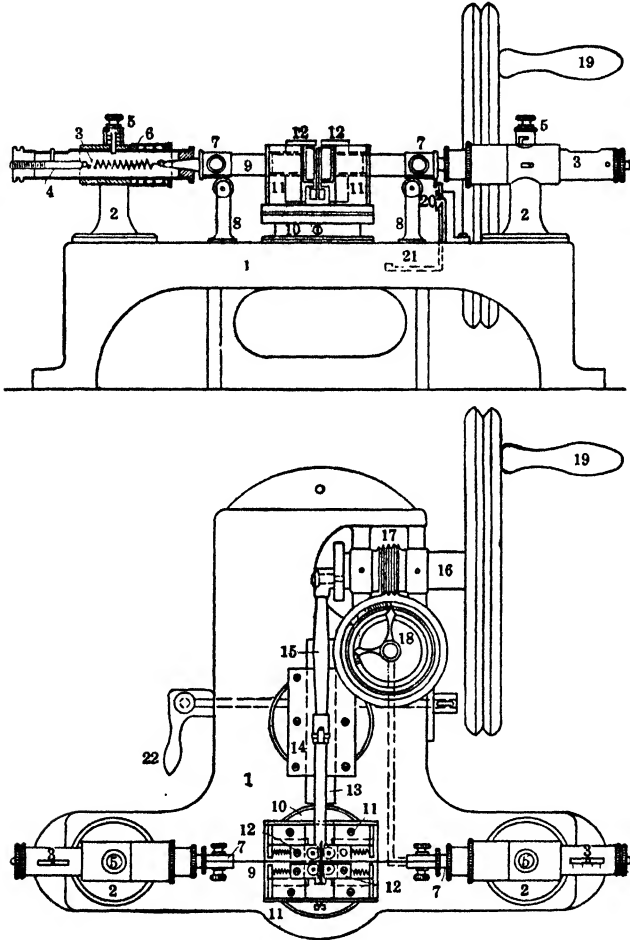
FIG. 61. SCHOPPER FOLDING TESTER.

should be multiplied by 16 and divided by the number of sheets in order to convert the results to a common basis. As this factor is not exact, the number of sheets actually used should be stated in the report.

Flexural strength is a useful test for boards, particularly fiber wall or insulating boards. A pendulum type of tensile strength tester may

be used by inserting in the clamps plates carrying stirrups, through which the specimen is placed. When the strip of board is thus suspended an increasing load is applied midway between the supports until the board breaks. Both the amount of the load required to break the board and its deflection at the instant of rupture should be recorded.
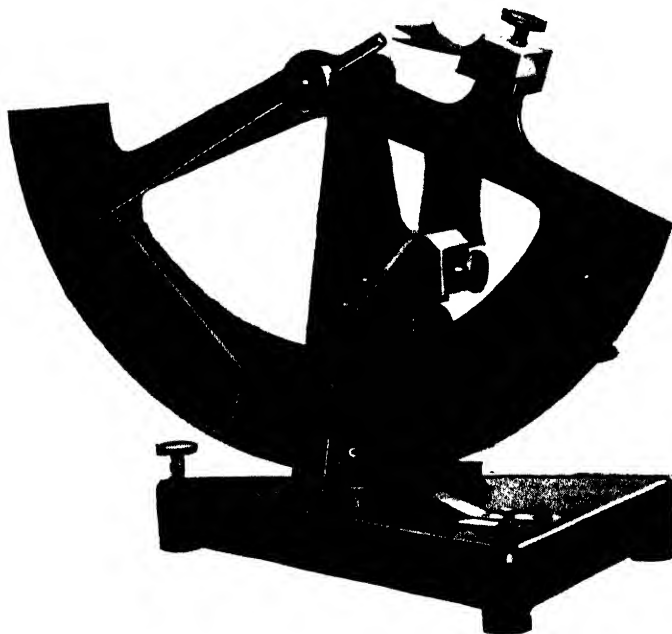
Courtesy Thwing-Albert Instrument Co.

FIG. 62.   ELMENDORF TEARING TESTER.

Stiffness. There are several types of testers for determining the stiffness of paper and paperboards. Most of them measure the force required to bend a strip through a definite angle, or the angle through which it must be bent in order to exert a given force at a designated point. The more common types measure the force by making the strip displace a pendulum as the strip is bent by hand. Another type measures the angle through which a strip of the paper will bend of its own weight when supported at one end.

Dirt. Dirt specks in paper not only injure its appearance but also cast suspicion on the quality of the paper as a whole, because they indicate careless manufacturing practices. The estimation of the amount of dirt, therefore, is one of the important tests in mill control

work, and many of the methods mentioned in the preceding chapter can be applied equally well to paper.

CHEMICAL TESTING

Moisture.[31]   In order to obtain comparable figures by calculating the results of chemical tests to a moisture-free basis it is necessary to determine the moisture content of the sample.   The usual way to do this is to weigh a sample of the paper into a weighing bottle with a ground-glass stopper, dry at 100° to 105° C., close the bottle, cool in a desiccator, and again weigh.   The loss in weight is assumed to be the moisture content of the sample.   Usually this is approximately correct, but as the air passing through the oven shares its moisture with the sample the sample never becomes completely dry and in damp weather the error may be quite appreciable.   The correction of this error involves the use of a vacuum dryer or of a tight oven through which dry air can be passed.   Larocque[10] shows that the residual moisture in oven-dried paper at 100° C. was 0.75 per cent when the room relative humidity was 80 per cent.   This is calculated on the basis that 120° C. in the oven and 20 per cent relative humidity in the room gave complete drying.

If the paper contains materials such as satin white or calcium sulfate, which lose water of crystallization at 100°, an entirely fictitious value will be given to the figure for hygroscopic moisture.   This again seems to indicate the use of a vacuum dryer so that the temperature can be kept low enough to avoid loss of water of crystallization.

In testing deliveries of paper and for control purposes, where large lots of paper are in question, it is necessary to take much larger samples.   These may be handled conveniently in cans having airtight covers, in which the samples are weighed both before and after drying.   To prevent any change in moisture during sampling the paper should be handled as rapidly as possible and placed in the can immediately.

Ash.[32]   The amount of ash in paper may be determined by igniting a weighed sample in a muffle furnace or over a Meker burner until no further loss in weight takes place.   The ignition should be at a low temperature at first in order to avoid as far as possible any reduction by carbon, and care must be taken to prevent loss by air currents.   Because of the greater speed of combustion a shallow dish is preferred to a crucible, and if a Meker burner is used a still further gain may be made by covering the dish with a curved platinum foil to deflect the heat downward onto the sample.

The ash may come from at least five sources: (1) materials in the pulps employed; (2) the loading or filling materials used; (3) substances used in coating or surface sizing; (4) mineral coloring matters; and (5) ash due to alum and size. The rag stocks and chemical fibers commonly used may contain about 0.10 to 1.9 per cent of ash, so a paper made without filler may contain as much as 2 per cent of ash. The ash in the body stock of a coated paper may be determined as usual after the coating has been removed by means of an enzyme, and the body stock dried, as described under " amount of coating."

The ash content of a paper must not be confused with the amount of mineral matter present as filler or in the coating. ¯A few of the fillers lose very little weight on ignition, but clay loses 12 to 14 per cent, crystalline calcium sulfate about 21 per cent, and calcium carbonates about 41 to 43 per cent. In order to convert ash to filler it is necessary to know what minerals were used so that the proper factors for conversion may be applied. This means that fairly comprehensive qualitative and quantitative analyses must be made and the results properly interpreted. In general the common methods of analysis are employed, but the details as applied to paper fillers and minerals have been assembled in three standard methods by T.A.P.P.I.[33] When one is thoroughly familiar with the minerals which are likely to be present it is possible to obtain considerable information by a few simple tests, but the compounding of fillers and coating minerals is becoming so complex that a complete analysis is frequently necessary. Even when that is finished the interpretation of the results is a matter of considerable difficulty and requires much experience.

Sizing Materials. In its broadest sense the term " sizing " is applied to various materials used in the beater, in the coating, and in surface treatments, and satisfactory qualitative tests must be able to distinguish between these substances and also to show the manner of application.

Starch is frequently used for all three purposes, and in the beater may be applied either raw or cooked. The presence of starch is shown by the blue or violet color developed when a dilute solution of iodine is added to the sample. It is well to confirm this test by boiling some of the paper with a little water, filtering, cooling, and testing the filtrate with a few drops of iodine solution. This is necessary because hydrocelluloses, which are only slightly soluble in boiling water, also give a blue color when brought into direct contact with iodine solution. Microscopic examination will show whether the starch granules have been burst by boiling or whether the starch was used without

cooking. If the paper is torn so that it splits on the edge and then is moistened with the iodine solution it is often possible to tell whether it is surface sized or not. If it is surface sized only, the interior of the sheet will remain white while the surface will turn blue; if considerable starch is used in the beater, it is partly cooked and drawn to the surface by the heat of the dryers so that the paper has the fictitious appearance of being surface sized. In case of doubt, microscopic examination of the paper after treating with iodine will sometimes help in forming an opinion, but will seldom supply proof.

Casein may be detected in paper by moistening the sample with Millon's reagent and warming gently. If casein is present a brick-red color will develop. In paper containing alkaline minerals, such as satin white or calcium carbonate, the alkali causes the formation of a yellow color and the characteristic test does not develop. In such a case the usual test may be obtained by moistening the paper first with dilute nitric acid, to neutralize the alkali, and then applying the Millon's reagent. This reaction is dependent on the presence of tyrosine, which is present in casein but absent in glue or gelatine, or present at most in doubtful traces.

Casein may also be detected by boiling the paper with 1 per cent caustic soda solution, carefully neutralizing the alkaline extract with nitric acid, adding Millon's reagent, and heating.

The Millon's reagent for this test may be prepared by dissolving 20 grams of pure mercury in 40 grams of pure concentrated nitric acid and diluting the solution to 180 cc. with distilled water.

Glue is sometimes used in coated papers and in small amounts in the beaters, but its chief use is for surface-sizing high-grade writing and printing papers. In the absence of casein, glue in appreciable amount may be detected by Schmidt's reagent,[34] which is prepared by dissolving 3 grams of pure ammonium molybdate in 250 cc. of distilled water and adding 25 cc. of dilute nitric acid (2 : 3). The reagent is not very stable and should be made up as needed. In making this test about 0.5 gram of the paper is boiled in 10 cc. of a 1 per cent caustic soda solution, filtered, and the filtrate neutralized with hydrochloric acid. One volume of Schmidt's reagent is then added to 2 volumes of the paper extract, and a white precipitate forms if glue or other nitrogenous matter is present. Unfortunately there is no reliable test for glue when casein is also present.

Rosin is used in beater sizing to impart water and writing-ink resistance to the paper. There is no single test for rosin which is simple and positive, but if an unmistakable test is obtained by both the

Lieberman-Storch and the Raspail methods[35] it is regarded as conclusive evidence of its presence. In the former, 1 gram of the paper, cut into small pieces, is placed in a clean, dry test tube, 5 cc. of pure acetic anhydride added, and reduced to about 1 cc. by boiling. The solution is then poured into a clean, dry porcelain crucible and cooled to room temperature. If waxy particles separate they are filtered off on a dry filter paper and a drop of concentrated sulfuric acid is allowed to run down the side of the container into the filtrate. A fugitive, rose-violet coloration at the junction of the acid and anhydride indicates the presence of rosin.

In the Raspail method the paper is placed on a glass or porcelain plate and a drop of strong sugar solution added. After a few moments the excess of sugar solution is removed with filter paper and a drop of concentrated sulfuric acid added to the spot. The development of a raspberry-red color indicates the presence of rosin; with unsized papers the color is brownish with only a trace of pink. This test is also given by albuminous materials, so they must be proved absent before positive conclusions can be drawn.

Rosin Determination. The quantitative determination of rosin in paper products is becoming more complicated and difficult because of the variety of fillers and sizing agents used. The older methods, which involved extracting the paper with alcohol acidified with acetic acid, gave incomplete extraction,[15] and the use of sulfuric acid was recommended. Launer[11] prefers hydrochloric acid and recommends extracting about 5 grams of the paper with 95 per cent alcohol containing 4 cc. of concentrated hydrochloric acid per liter. The extraction may be made in a Soxhlet or Underwriters' extractor for 2 to $2\frac{1}{2}$ hours at the rate of 15 siphonings per hour. The solvent should then be evaporated, the residue dried at 100° C. for 15 minutes, and, after cooling, 20 cc. of anhydrous ether added. If the rosin is seriously contaminated with other materials it may be necessary to scrape it with a stirring rod and filter the solution through a dry filter paper. The filter and extraction flask from which the rosin was dissolved must be thoroughly washed with anhydrous ether. The combined filtrate and washings are warmed to about 40° C., preferably under reduced pressure, until the ether has evaporated, and the residue is dried for 15 minutes at 100° C. and weighed as rosin.

If the paper contains fillers which react with acid, such as ZnS, $CaSO_3$, or $CaCO_3$, it should be weighed and then treated with N hydrochloric acid, washed, and dried before making the extraction. If paraffin or similar waxes are present it may be necessary to weigh the rosin and wax together, then saponify with alcoholic potash, ex-

tract the wax with ether, and deduct its weight from the total, thus obtaining the weight of rosin by difference.

Even with the best methods at present available the determination of rosin cannot be considered as having a high degree of accuracy.

Starch Determination.   The methods for the determination of starch in paper are in a rather unsatisfactory state and none can be recommended as particularly accurate. The method of Voorhees and Kamm[42] depends on the hydrolysis of starch to reducing sugars by means of acetic acid, but their method applied to soda fibers and groundwood shows a starch content of 0.5 to 0.8 per cent, even when none was present. This, and the possibility of similar though smaller errors when sulfite pulps are used, makes the method of extremely doubtful value, especially when small amounts of starch are in question.

Considerable study has been given to the use of diastase, particularly saliva diastase, for the separation of starch and cellulose, and apparently very good results have been obtained. The best pH for conversion is 6.7 to 7.0, and the presence of sodium chloride aids the reaction. When no blue color develops on addition of iodine solution all the starch has been converted to maltose. This is then separated from the fibers by filtration and washing, further converted by boiling with hydrochloric acid, and the reducing sugars determined by means of Fehling's or Benedict's solution.

Glue and Casein Determination.   A determination of either of these substances depends on a determination of the percentage of nitrogen and the conversion of this into glue or casein by means of a factor. The usual Kjeldahl or Gunning[36] methods determine nitrogen with entire satisfaction, but the conversion of nitrogen to casein involves so many assumptions that the final result is in very serious doubt. The nitrogen content of casein is by no means a constant for commercial air-dried products and not so very much better if it is calculated on the moisture-, fat-, and ash-free basis. The factor 7.85 may be taken to convert nitrogen into commercial casein, but this may be in error by as much as 8 to 12 per cent of the actual casein used. Then there is the possibility that the stock for making the paper to be coated contained some waste papers with casein on them, or a glue size may have been used in their preparation, and both of these would contribute to the nitrogen content and cause very serious errors when it is calculated to casein. Then again there is the question of how much of the ammonia used as a casein solvent remains in the finished paper to contribute to the error. Considering these possible sources of error, and the fact that none of them can be checked for probability or

magnitude when the paper under test is of unknown origin, it is obvious that the accuracy to be expected is not very great.

Alpha-Cellulose.[36]   The alpha-cellulose determination in papers depends on the same principles as that for pulps.   The method is admittedly not applicable to papers containing highly lignified fibers, and the results must be corrected for moisture, fillers, rosin, glue, or starch sizings, and any other material which may be present in sufficient amount to cause an appreciable error.   Considering the difficulties in determining these constituents and the assumptions which have to be made in calculating the corrections, it appears that the final result can be only an approximation and that only large differences should be considered in drawing conclusions.

Amount of Coating.   The method to be employed in determining the amount of coating on a paper will depend on the adhesive used and the subsequent treatment given the paper.   If the adhesive matter is starch, or any other readily soluble substance, it is sufficient to soak the sample in warm water, remove the coating by careful brushing with a soft brush, wash with water, and dry.   The difference in weight will represent the coating removed.   If the adhesive was casein it may be sufficient to substitute a solution of ammonia for the water, but if the casein was waterproofed by means of formaldehyde this treatment may have no effect.   In such a case the paper may be soaked for an hour at 50° C. in a solution of some enzyme and the coating removed as before.   A solution of 1.5 grams of trypsin and 25 cc. of 0.1 N NaOH in a liter of water has been found effective, but there are others which are claimed to be more rapid in action, less expensive, and more stable.   Of these, Degoma D. L. made by Röhm & Haas Co. is said to be particularly suitable.

This method is not effective for papers which have been given a lacquer or similar finish over the coating, but it may be applied if the lacquer can be removed.   Frequently this may be done by extracting the paper with ethyl acetate or other solvent before applying the enzyme.   This causes a slight error by removing resins, waxes, or similar materials which might be present in the body stock or coating, but this is not usually considered serious.

Paraffin Determination.[37]   This is of importance in waxed wrapping papers and those in which rosin-wax sizing agents are used.   The amount present may be determined by extracting the paper with carbon tetrachloride in an extraction apparatus such as the Soxhlet or Underwriters.   The extract should be evaporated to dryness, 25 cc. of 0.5 N alcoholic potash added, and the mixture again evaporated to dryness, taken up with ether, and transferred to a separatory funnel.

The final volume of ether should be 25 cc. and that of the water 150 cc., and a small amount of sodium chloride should be added to prevent emulsification. After shaking thoroughly and allowing to stand, the water is drawn off into a second funnel and again extracted with ether one or more times. The combined ether extracts are washed with 100-cc. portions of water until the liquids separate clearly; then the ether extract is evaported to dryness, dried at 100° C. for 1 hour, and weighed.

Acidity Determination. This is of importance because of the relation of acidity of the paper to its stability and to the effect which the paper may have on materials with which it may come in contact. According to Kohler and Hall[9] the acidity of paper may come from the alum or acid rosin precipitant or from alum used with the glue in surface sizing. They term the former " internal acidity " and consider it injurious to the durability of the paper; the latter, or " external acidity," they consider almost harmless. Papers may range from strongly acid to quite alkaline from the presence of an alkaline filler such as calcium carbonate. Some coated papers may even be alkaline on the coated side and acid in the body stock. Since alkalinity in a paper increases its stability no attention has been paid to its determination, but much study has been given to methods for acidity.

Total acidity[39] may be determined by heating 5 grams of the ground paper with 250 cc. of water at the temperature of a boiling water bath for 1 hour, separating the solution from the fibers on a Büchner funnel by strong suction, cooling rapidly, and titrating as soon as it reaches room temperature, using 0.01 N NaOH and phenolphthalein as indicator. Two more extractions should be made in the same way, and the total alkali used for the three titrations considered as representing the acid present in the paper. It is customary to calculate this as sulfuric anhydride equivalent to the alkali needed.

Acidity or alkalinity in terms of hydrogen-ion concentration (pH) is best determined by means of the glass electrode, using 1 gram of the finely cut paper soaked in 70 cc. of water at room temperature for about an hour.[12] The unfiltered mixture is used for the test. It is generally admitted that colorimetric methods, or those using a quinhydrone or antimony electrode, are not accurate enough to be of much value in testing paper extracts.

The term " pH " is commonly used to denote the degree of acidity, or the concentration of hydrogen ions, of a substance. For example, tenth normal acetic and hydrochloric acid solutions would contain the same total acid by titration, but the degree of acidity of the hydrochloric acid would be much the greater.

On the pH scale the neutral point is placed at 7; as the acidity increases the pH value drops, while on the other side of neutrality, increase in alkalinity is indicated by increasing pH values. As the scale is logarithmic, each change of a full unit on the scale means a change of ten times in the acidity. A recent paper by Booth[1] presents some very interesting facts regarding the methods of expressing hydrogen-ion concentrations and the importance of fully understanding their meanings.

Sulfur and Silver Staining. Papers which are to be used to wrap silverware must be proved free from sulfur compounds or other materials which may cause stains. This may be done by wrapping a piece of smooth, highly polished silver, or silver-plated ware, in the paper to be tested. The paper should be wet with distilled water when applied and should be in close contact with the metal surface for at least 3 hours, during which time it is slowly drying out. If two flat plates are used and the paper placed between them a drying time of 3 hours at about 160° F. should give good results. The oven in which the test is made must be temperature-controlled and protected from access of laboratory fumes. This practical method of testing is capable of wide variations in its application, and no generally accepted procedure has yet been worked out.

In distinction to this are the chemical methods for determining the presence of sulfur compounds which may cause staining. The T.A.P.P.I. method[40] suspends 0.25 gram of the paper in water, adds 2 grams of aluminum foil and 10 cc. of concentrated H_3PO_4, and heats on the steam bath for an hour. The flask is so arranged that the evolved gases must pass through a piece of filter paper moistened with lead acetate, and the depth of stain is indicative of the amount of sulfur present. This test is objectionable because of the small size of the sample and because sulfur compounds which may not cause staining are reduced by the treatment with the evolution of hydrogen sulfide.

These objections have been overcome by Ohlwiler in a method developed by the American Optical Co. The apparatus consists of an Erlenmeyer flask with a side tube containing a stopcock through which acid may be added, and a delivery tube 20 mm. in diameter at the top and with a large bore and long bevel at the bottom so that vapors will not contaminate the test cloth. This cloth consists of a piece of batiste, sensitized by dipping into a slightly acid solution of lead acetate and drying; it is fastened over the top of the delivery tube so that evolved gases must pass through it. The test is carried out by placing 2 grams of the paper to be tested in the flask with about 50 cc. of water and bringing the contents to a boil. When the air has been

expelled 5 cc. of dilute sulfuric acid (1 volume H_2SO_4 with 3 volumes water) is added through the side tube and stopcock and the boiling continued for about a minute, after which the cloth is examined for staining. A sulfide content equivalent to 1 part per million of sulfur gives a decided stain, and a positive test by this method is considered cause for rejection.

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PRINTING

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A discussion of printing should include the subjects of paper and ink and their interrelationship, as well as the processes by which they are combined by the printer into a finished job. To do this in sufficient detail to make it equally valuable to the paper maker, ink maker, and printer is quite impossible in the space available, and probably beyond the capacity of any single individual; therefore the plan followed in this chapter is to view the subject with the eyes of the paper maker, giving a brief description of the major printing processes, followed by such notes as it has been possible to gather on inks and papers and their requirements. It is hoped that the facts given may suggest reasons for some of the complaints against paper and possible means for avoiding troubles.

The chief object of printing is to reproduce type matter and half-tones with accuracy, and commercially this also involves considerations of quantity and cost. The problem is theoretically possible of solution either by developing a printing process which will be successful on any kind of paper or by producing a paper which will print satisfactorily by any process. As neither solution is yet in sight, it is important for the ink maker, printer, and paper maker to combine in working out their mutual problems.

Modern printing is divided into three main classifications: (1) letterpress; (2) planography, which is offset or lithography; and (3) intaglio, including rotogravure. Each of these has subdivisions with widely differing requirements for both ink and paper.

Letterpress or Relief Printing. This is the oldest, best-known, and most widely used method of printing, and, as its name indicates, the areas which are to print stand out in relief from the rest of the form or plate.

Printed matter produced by this process includes type and pictures. The preparation of type need not be discussed, but a brief description of the method commonly used in preparing pictures for reproduction may be of interest. This is known as the half-tone process because in its use about half of the tone values of the original are lost, so what remains is a " half-tone."

For the preparation of half-tones a " screen " is necessary. This is prepared by coating a sheet of glass with a wax composition and then with a diamond point ruling diagonally upon it fine parallel lines at exactly equal distances apart. The plate is then treated with hydrofluoric acid, which etches the glass wherever the wax was removed, and after cleaning the plate an opaque, dark pigment is rubbed into the lines. Two such plates are sealed together face to face, with the rulings at right angles, to form the finished screen. The number of lines per inch varies from 50 for very coarse work to 300 for the finest.

What is termed a screen negative is prepared by placing this screen in a camera, in front of and near the plate, but not in direct contact with it, and then photographing, through the screen, the picture, drawing, or photograph to be reproduced. The lines prevent the passage of light, and the resulting negative consists of innumerable dots separated by the unexposed spaces which were covered by the lines.

The metal plate which is to form the half-tone block is sensitized with a mixture of gelatine or albumen and bichromate of potash, dried, and exposed under the screen negative just as in ordinary photographic printing. Copper is used for the best plates; zinc is standard in newspaper work. The exposed plate is then washed in water which dissolves the gelatine film wherever it has not been exposed to light. This gelatine picture is heated and burnt onto the metal like an enamel which protects the metal at these points during the etching. This is done by treating the plate with ferric chloride solution which dissolves away the exposed copper, thus leaving the picture in relief. In order to produce the best results the plate must be re-etched locally, and it is in this operation that skill and judgment are most necessary on the part of the plate maker. Table 73 shows the standard depths for half-tone plates in thousandths of an inch.

TABLE 73

Tone Values	55-Line Zinc	85-Line Zinc	100-Line Zinc	100-Line Copper	120-Line Copper	133-Line Copper	150-Line Copper	175-Line Copper
High lights	8	4.6	3.2	2.6	2.5	2.3	2.2	1.8
Middle tones	5	3.1	2.2	1.8	1.7	1.6	1.4	1.0
Shadows	3	2.2	1.4	1.0	0.9	0.9	0.9	0.6

Process printing in three colors, or more commonly three colors and black, requires separate half-tones for each of the colors yellow, red, blue, and black. Color filters are used in making these half-tones, and the screen is set at a different angle for each in order to prevent

the dots in the successive colors falling on top of each other in straight lines. If a single-color half-tone is to be made the screen is set at 45°.

Original plates are seldom used where any large number of impressions are to be made as they soon wear out; also any damage to the plates necessitates the making of entirely new ones. The use of electrotypes or stereotypes obviates this difficulty. Stereotypes are made by taking a papier-mâché mold of the original form and then preparing castings from this. Such plates are used chiefly for newspaper work or the cheaper class of "pulp" publications. Electrotypes giving a more accurate reproduction of the original form, are prepared by coating the original with a thin film of graphite and then taking an impression of its surface in wax or gutta-percha. The graphite prevents sticking and allows the plate to be removed from the wax, which is then placed in a bath of copper sulfate and coated electrolytically with a film of copper. Deposit of copper may be continued until it becomes thick enough to use as a plate, or a thinner film may be backed up by type metal. This process allows any number of electrotypes to be prepared from the same original, which insures a sufficient supply of plates for even the largest editions. Where excessive wear is expected they may be faced with nickel by electrolytic means and are then sometimes called "steel-faced."

In making electrotypes the metal is deposited into the mold, while if stereotypes are faced with nickel the metal is deposited on the plate itself. This causes loss of detail in stereotypes but not in half-tones, since the size of the dots and the depth of etching remain the same in the half-tones.

When electrotype plates are mounted on wood blocks to bring them to the right height the effect of humidity changes on the wood brings in problems which are very similar to those of paper and moisture.

Planography. This process originally printed from stone, hence the name "lithography," but stone has been replaced almost completely by the equally good and less cumbersome zinc and aluminum plates. All parts of the plate are in the same plane and all come in contact with the paper, and as the plate is rolled with two sets of rollers, one wet with water and the other with ink, the process requires that the printing areas be made ink receptive and water repellent, and the reverse in the non-printing areas. In direct lithography the plate comes in direct contact with the paper, while in offset printing the ink is transferred from the plate to a rubber blanket, and is then "offset" from the blanket to the paper. In this country direct lithography is confined almost entirely to poster printing, and even in that field the

offset process is used to some extent. Direct lithography, however, gives greater clarity and sharpness of print than the offset process.

The half-tones used in lithography are made on the same principle as those for letterpress printing. Type matter to be used must be set up in a form and a print made; this is then photographed, the resulting film negative properly assembled with those of the half-tones to be used, and the whole printed on a sensitized zinc of aluminum plate. The plate is prepared for printing by " graining " with marbles, sand, and water to give the surface a slight " tooth " which furnishes an anchorage for the sensitizing film and also makes the surface receptive to water wherever the film is removed. After this the sensitizing, printing, and developing follow very closely the methods outlined under letterpress printing.

Intaglio Printing. In this process the areas which are to print are etched or engraved into a plate or cylinder. A heavy ink is smeared over the plate and the excess wiped off, leaving the engraved areas still filled with ink, from which it is removed by the paper as it passes through the press. Steel engravings, as exemplified by paper currency, are typical of intaglio printing.

Rotogravure, such as the Sunday newspaper supplements, is a sort of stepchild of the old intaglio process, the design being etched into copper cylinders instead of steel plates. In preparing the illustrations and plates for rotogravure a different type of screen is used whose fineness is greater than that in letterpress or offset printing on papers of the same finish. A fundamental difference between rotogravure half-tone printing and that done by other processes is that the varying gradation of tones is obtained by differences in depth of etching in rotogravure, and by variation in the size of the dots in the other printing processes.

Rotogravure printing differs greatly from other processes. The etched cylinder revolves in a bath of fluid ink, the excess is wiped off with a " doctor," and the cylinder revolves against another of relatively hard rubber, around which the web of paper passes during printing. The paper removes the ink from the depressions in the plate by a blotting action.

Printing Inks. The kind of ink to use on any given job depends on the character of work, and on the kind of paper, and press. Its selection is a matter for the printer and the ink maker, and its properties must be such that it will print and dry properly on the paper for which it was made. Ink is a very complex mixture which it is practically impossible to analyze with any degree of completeness, and the figures which can be obtained are not easy to interpret. No an-

alysis which can be made will tell whether an ink will print well, or in case of trouble, whether the ink was at fault.

The ordinary types of ink are composed chiefly of pigments and oily carriers or vehicles. These range from high-grade oxidizing varnishes for use with engravings, to low-grade non-oxidizing oils for newsprint inks, and to these ingredients are added other materials such as dryers, softeners, and oil-soluble colors, each of which imparts certain properties to the ink and makes it suitable for some particular kind of work. Newsprint ink, for instance, dries by absorption and is not suitable for high-grade book or magazine work, even though used on a web press. Lithographic and process inks dry principally by oxidation, while book and magazine inks dry by a combination of absorption and oxidation. Rotogravure inks dry by evaporation, as do also the newer kinds of web-press book and magazine inks known as " heat-set " inks. Inks can be modified to overcome troubles caused by defective or non-uniform paper, but only at the expense of the quality of the finished job. Except for rotogravure, the cleanest printing, either letterpress or offset, is done with inks that are as stiff and tacky as the process and paper will permit; rotogravure ink is thin and has practically no tack.

Special types of ink are sometimes used to obtain certain specific results. Double-tone inks contain an oil-soluble dye in addition to the usual pigment, and as the oil is absorbed by the paper it spreads beyond the area covered by the half-tone dot, or type, and the color carried with it gives a two-tone effect. These inks were formerly quite popular, but were very sensitive to the quality of the paper, and as good results were not at all certain their use has largely been discontinued.

Metallic inks, commonly known as gold or silver inks, contain brass or aluminum powder of varying shades. These pigments, particularly the golds, tend to react with the fatty acid constituents of the vehicle and become dull, so such inks are usually mixed immediately before use. Their particles are flat and have considerable covering power, tending to lie like shingles on a roof. The vehicle consists of a mixture of lithograph varnishes, resins, oils, and dryers similar to those used in ordinary inks. It has been found best in gold inks to use about 60 per cent of powder and 40 per cent of vehicle by weight, and to keep this ratio constant. The heaviness of the vehicle should be in inverse proportion to the ink-setting time of the paper used.

Metallic inks work best on papers having a good surface ink receptivity and a high density. The former insures removal of sufficient ink from the plate and the latter keeps the vehicle near the surface where it can act as a binder for the metallic particles and keep them

from powdering and rubbing off. A high printing smoothness is also necessary with these inks; poor results may be due to scattering of the light from rough surfaces rather than to poor coverage with the metallic particles. On hard-surfaced papers, such as litho coateds, the results with metallic inks are much improved if the paper is first printed with a base ink of suitable color to blend with the metallic ink.

One of the newer developments in printing ink is the " heat-set " ink, which is sold under various trade names. The vehicle for this type of ink is primarily a natural or synthetic resin dissolved in a volatile solvent; lithographic varnish, if present at all, is in very small amount. Since heat is essential in the drying of such inks, their use is limited principally to web presses where the printed web may be led through a complicated system of heating chambers, followed by cooling rolls. Their drying time under such conditions is a matter of seconds, but not all the solvent evaporates during this heating period. Some of it is driven into the paper, from which it evaporates later, but for all practical purposes the ink is dry when the paper leaves the press. Any paper which will print well on a web press with oil-base inks will give good results with heat-set inks and, in addition, papers which are not absorbent enough to allow web-press printing with oil inks can be used satisfactorily by the newer process.

A still newer ink, as yet in the development stage, is a cold-set ink, which is solid at normal temperatures but assumes the consistency of ordinary printing ink when heated. Special equipment is needed, since ink fountains, rollers, ink plates, and printing plates must all be at a temperature to maintain ink fluidity until the impression is made. This ink shows promise, as the initial installation cost would probably be smaller than for heat-set inks, the cost of operation should be less, and the fire hazard and possible damage to paper completely eliminated. Its most obvious defect is its tendency to soften when warm, and to smudge and come off on objects in contact with it.

Water-color inks[3] have a glycerine base instead of oil, and in common with oil inks they dry lighter in color than when wet. For a given depth of color the ink consumption is often less than for the same colors in oil inks. These inks set immediately and tints will dry in an hour, though opaque inks may require as much as 6 hours. Because of their composition they penetrate somewhat into rollers containing glycerine and the color may work out later and cause off-tints. They work well with rubber plates, and such plates do not disturb the texture of the paper. Oil inks will print satisfactorily over water-color inks, but not vice versa. For water-color printing mat finish papers are preferred, though antique, English finish, and super papers

also work well. Coated paper is considered undesirable because it sometimes changes the color of the ink. When smooth papers are to be printed it is possible to use metal instead of rubber plates.

Multicolor web printing, whether in two or more colors at a time, involves the use of inks of varying degrees of tackiness, the first applied being more tacky than the second, and so on up to the limit of the colors applied. In this way each ink is able to lift the following ink off the plate. If the inks are not much different in tack, or if the order of tackiness is reversed, the second ink would tend to pick the first off the paper, resulting in " mixing " and distorted, muddy colors. Inks which lift from the plate properly are said to " trap " each other.

According to Hoch,[3] the laying qualities of the ink as well as the uniformity of the color are influenced by the quality of the rollers. Old, hard, lifeless, or uneven rollers increase the ink consumption necessary for uniformity in color. Coverage is also dependent on the specific gravity of the ink and on the type of paper surface. For very open, light forms the consumption of black ink would be about as follows for 1000 impressions of 100 square inches each:

	POUND
Coated papers	0.047
Supercalendered	0.052
Machine finish	0.074
Rough	0.102

Regarding the chemical properties of an ink, it is claimed by Tritton[7] that an ink containing no free fatty acid cannot produce an image which will accept ink and reject water, but that one with as little as 1 per cent of fatty acid can do so. These acids cause the image on zinc to have more tendency to spread than that on aluminum, and a higher fatty acid concentration is desirable for aluminum plates. Any substance added to an ink which reduces its acid value to less than 8.0 will reduce its image-forming capacity; in practice, magnesia in ink is found to remove the image from the stone or metal plate.

Bowles[2] has presented an interesting paper entitled " Printing Ink as a Dynamic System," in which he traces a typical ink through its various stages of manufacture and use, and claims that any study of the performance of inks must include consideration of their whole history. He seems to feel that any investigations involving empirico-statistical methods, such as the use of printing presses, are likely to give very misleading results and that, conversely, an understanding of the basic facts of the printing process is quite likely to lead directly to useful practical applications.

Paper from a Printing Standpoint. No one kind of paper can be suitable for all kinds of printing, and in fact the same kind of paper is not always satisfactory for two divisions of the same printing method, particularly letterpress. Most of the factors relating to printability have been given little or no attention until recent years, and even now knowledge along this line is not too reliable.

In looking at paper from a printing standpoint it should be considered, not as a finished product, but as a raw material which must possess certain definite characteristics in harmony with the process by which it is to be printed. The paper maker, on the other hand, judges paper more or less as a finished product on the basis of such considerations as furnish, formation, basis weight, and various physical tests, none of which measures printability directly, although most of them have some bearing on it.

Printing characteristics of paper involve first of all formation. This is of more importance to the printer than to the paper maker, for unless a paper has good formation for its particular grade all the results obtained with it will be inferior, no matter how well it may qualify in other respects. Unfortunately formation is one of the characteristics for which no method of numerical measurement has yet been developed and generally adopted in the paper industry.

Other factors which influence printability are opacity, density, printing smoothness, surface strength, and ink receptivity. Rosin sizing is not a factor of importance in connection with ink receptivity, as printing ink will penetrate a rosin-sized paper as readily as, or even more readily than, an unsized paper. The relative importance of the other factors varies in the different kinds of printing and with the papers used, and the correct values of each can be determined only after consideration of many things, among which are (1) the speed of the press; (2) whether sheet fed or roll fed; (3) the number of colors to be superimposed wet; (4) the kind of ink to be used; (5) the fineness of the half-tone screens; (6) subsequent requirements in bindery operations, and sometimes use requirements, as in package wrappers and labels.

In considering the question of specifications for paper it has been remarked that the only way to tell how it will print is to print it. Lacking facilities for printing by the numerous processes which are applied to his products, the paper maker must depend upon such other tests as smoothness, oil penetration, porosity, and tests indicating the strength of the paper surface, as the wax test, all of which have a bearing on the printing processes. If such tests are correlated with those of a considerable number of papers which are known to have

given satisfactory printing results they will form a basis for building up specifications along these lines, but in reality they are measures of the uniformity of the factors affecting printing, rather than the actual printability of the paper. Under no conditions will they enable a person to test papers and be certain that they will print well or poorly.

Uniformity is the most essential characteristic in any printing paper, whether it be newsprint, No. 1 enamel, or any of the numerous grades between. Good printing can be done under certain conditions on either an ink-resistant or an ink-receptive sheet, provided the paper runs uniformly one way or the other, but under no circumstances can it be done if the paper varies widely from sheet to sheet.

Obviously the specifications for each grade of paper and kind of printing must be ascertained separately, which means that they are most valuable for a mill making only a few standard grades for definite purposes. Once established, they should be adhered to closely, since one factor cannot be given undue consideration without adversely affecting some of the others. Printing smoothness is probably one of the best examples of this. Increasing the smoothness considerably above the determined range might improve the paper, in the opinion of the paper maker, but it might add nothing to the clarity of the print, though reducing the ink receptivity and opacity of the paper and causing offset and excessive show-through.

Fortunately, printing processes are flexible enough to take care of the normal variations in properly made paper; the trouble comes when they are too wide and occur from sheet to sheet or irregularly in any given delivery. When adjustments in the printing process have to be made they are planned to take care of the worst of the paper, hence this part determines the quality of the finished product. An essential part of drafting specifications for printing paper consists, therefore, in determining the range of each characteristic within which the printer can get uniform results, and then correlating the various factors so that there may be no conflict between them.

Of the factors to be considered in drawing up specifications, that of ink receptivity, is influenced by the type of press and of the ink used. Roll-feed or " web " presses are used in all kinds of printing, but lithographic presses of this type are not often used in this country, and then chiefly for specialty printing, such as labels. Web presses usually print both sides of the paper in one passage through the press and deliver the work in folded signatures of 4 to 32 pages. Sheet-fed presses, on the other hand, usually print but one side at a time, deliver the sheets flat, and run at much slower speeds. To avoid offset and smudging, web-press paper must be more ink receptive than that for

sheet-fed presses. The kind of ink used also has a bearing, and even with " heat-set " inks the paper must have a high surface ink receptivity to insure the removal of enough ink from the plate to give a satisfactory color to the finished job.

Press speeds and the number of colors to be superimposed wet are the main factors to consider in determining the necessary surface strength of the paper. The openness or heaviness of the form being printed is also a determining factor. Higher press speeds require greater surface strength in paper to enable it to resist picking, and as presses are constantly being speeded up this requirement will be still more important in the future.

The necessary printing smoothness of the paper is closely connected with the fineness of the half-tone plates used. If the paper for the job is chosen first the half-tones are made of a fineness to harmonize. In book and magazine work it has been found that the combinations of paper and half-tones shown in Table 74 will give the best reproduction and cleanest printing in production runs.

TABLE 74

Kind of Paper	Fineness of Screen Lines per Inch
B grade MF and EF	100
A grade MF and EF	100–110
B grade Super	110
A grade Super	120
Coated	120–133

The use of too fine a screen is a common fault; screens finer than those mentioned can be printed, but on production runs the results will not be so good. The paper must be smooth enough to permit each dot to print cleanly and undistorted; if it is too rough for the screen used the printing will be muddy, as the inequalities in the paper surface will not allow the full area of the dots to make contact with the paper.

Mechanical Imperfections. Regardless of the kind of paper or the type of printing, mechanical imperfections in the paper cause troubles, among which are the following.

Poorly wound rolls develop wrinkles when going through the press, spoiling the printing and frequently smashing the printing plates. Variation in tension due to soft spots or soft-end rolls results in misregister when two or more colors are printed and also causes defective folding. When heat-set inks are used, a " floppy " web, due to poor winding, sometimes hits the burners and causes a fire. Web breaks,

with consequent loss of production, may be caused by widely varying tension across the width of a poorly wound roll, but as a rule, they are caused by slime spots, calender cuts, hair cuts, and turn-ins. With press time costing from ten to twenty-five dollars per hour, the presence of such defects in rolls may easily cause the loss of all the profits on a job.

Stuck splices invariably cause web breaks. If the splices are too thick, the printing plates may be battered by the excessive pressure developed when they pass between the plate and impression cylinders, and a shutdown for plate repairs or replacement is then necessary. Too much overhang at splices may result in the excess paper folding back over the splice, with the same effect as a thick splice. When heat-set inks are used the overhang may flare out from the web and catch fire as it passes the burners. At the best, this makes rewebbing the press necessary, causing a delay of half an hour or more according to the kind of press.

When a splice goes through a press the colors frequently fail to register until it has gone completely through, so an excessive number of splices, even though all are properly made, results in excessive waste. This is particularly true in multicolor rotogravure printing. In this case the press must be slowed down until the splice has gone through, and changing the press speed changes the tension on the web, with consequent misregister of printing. Each splice in a roll of paper used on such a press results in a loss of about 60 linear feet of the web.

Loose scraps of paper wound in rolls tend to batter the plates and as a rule also cause web breaks. At the best, such scraps cause from 10 to 20 minutes' loss of press time, and when the plates are battered, hours are often required for repair or replacement.

In flat stock, mechanical defects result in lost time and production. If the paper is not flat it will neither feed nor deliver properly. Cockles cause some feeder trouble, but their greatest fault is misregister in spots when multicolor work is being done. Excessive cockling may also cause wrinkles when the paper goes through the press.

Torn and short sheets interfere seriously with the action of the automatic feeders, and when they get in the press battered plates usually result. If the paper is of such a quality that it takes a permanent set as it pulls away from the cylinder the feeding for a second impression is interfered with.

Conditioning paper to match pressroom conditions minimizes misregister as well as feeder and delivery troubles, but conditioned paper in an unconditioned pressroom usually causes more trouble than if the paper had not been preconditioned. Such paper as a rule contains

more moisture than is necessary to match the average unconditioned pressroom atmosphere. As a result it dries out around the edges, developing " tight edges " and leaving a fullness in the center of the sheets which runs into wrinkles at the back edge or back corners as the paper goes through the press. Tight edges can be corrected to some extent by dampening the outside of the pile and allowing time for the moisture to work into the sheets. In bad cases, a better method is to hang wet cloths around the pile overnight. Although these methods will usually enable the paper to be printed once, they will not help the misregister that occurs if the paper is put through the press a second time, as is done in many multicolor jobs. This misregister is due to shrinkage of the sheets caused by moisture evaporating from the surface while going through the press. There is no cure for this trouble.

Picking is a defect which may occur in any paper and is caused by lack of surface strength. On uncoated paper it shows as a lifting of the fibers in bunches, usually on the heavier parts of the print. This causes a white spot where the pick occurred, usually followed by a black spot surrounded by a white ring on subsequent prints. At times the surface of the paper may lift in large sections, which may or may not pull entirely off the sheet, but usually it shows as a blistered appearance rather than a complete separation of the surface.

In coated papers picking may be due to the coating parting from the paper, because of too little adhesive, or the body stock may give way from structural weakness. So far as the printer is concerned the result is the same, but the paper maker must know which happened in order to correct the trouble in future runs. Coating picks are often confused with spots caused by particles of dust and dirt on the surface of the paper. These may be distinguished readily by examination under a strong lens, which shows the coating to be intact if the spot was caused by dust.

Picking may also be caused by too tacky an ink, and this in turn may be due to a low temperature in the pressroom. Picking on multicolor presses often occurs at the start of a run because of cold plates, rollers, and ink. Tests on coated papers have proved that a paper to be printed at 75° must be much stronger in regard to coating adhesive than if the pressroom temperature is kept at 85°, and many a paper is blamed for weakness because it happened to be printed on a Monday morning in a relatively cold room. Proper adjustment of the tack in the ink, and slowing down of the press, will do much to prevent picking, but slow running is undesirable from a cost standpoint. Softening of the ink is best done by adding a softer ink of the same color; this

does not reduce the color strength of the ink as do kerosene, wax compounds, and soft varnishes and oils.

Paper on which two inks are to be superimposed wet must have a higher surface strength than that used for one ink alone, and that for four inks must be stronger than that for two. A paper may appear strong enough for the first ink, but still be so weakened that succeeding inks may cause picking, in spite of their lesser tackiness. Usually the minimum surface strength of paper is sufficient for two colors wet, but consideration must be given to the nature of the printing, as the tendency to pick is much greater in solid areas than in screen surfaces of the same size. If it is necessary to soften the ink to avoid picking, each of the succeeding inks must be softened, in order to maintain the correct difference in tackiness. This may overcome picking, but the printed results are never so sharp and clear as they would have been with inks of normal tack.

Rotogravure inks have little tack, and although all are applied on the same trip through the press, each is dried before the next is applied, so no question of additional surface strength is brought in.

Complaints and Defects. It is extremely difficult to separate troubles due to ink from those caused by the paper, or by some act of the printer, who often insists on " doping " his ink after trouble develops, or even in anticipation of it. It seems best, therefore, to treat the subject collectively rather than try to separate it into its various components.

There are, of course, many defects which may be present in paper to cause the printer serious trouble, and some of these are so obvious as hardly to need mentioning. Among these are fuzz on the surface and loose dirt or trimming dust on the paper. These cause filling up of cuts and type and make it necessary to wash up frequently. Complaints of this nature should be looked into carefully as it is often found that the fibers which collect are entirely different from those in the paper being used, in spite of which the paper is held responsible. A somewhat similar trouble, though not so easily detected, is caused by the ink picking the filler off the paper when the latter is too heavily loaded or the fibers not beaten enough. This makes the plates fill up and give very unsatisfactory prints.

Differences between the wire and felt side of the paper frequently cause variations in the printed results. This is much less troublesome than formerly because of the improved processes of paper making.

The drying of the ink is sometimes so slow that complaint is made regarding the quality of the paper, but nine times out of ten this is an ink trouble and the paper is not at fault. The only qualities in paper

which are known to retard drying are lack of porosity, and in coated paper too much of certain oils or waxes in the coating. On the other hand an ink can be made which will dry satisfactorily on any given paper, but not necessarily on all.

If an ink will not dry on a paper for which it was made it may be because of too much or too little dryer. It is difficult to determine which is the cause, but it is far more often due to insufficient dryer, for which the cure is to add more. If an ink contains too much light-bodied varnish, it may soak into the sheet to such an extent that the pigment retains an insufficient amount to bind it to the paper and so it chalks or rubs off.

Instances are known where the proper ink was supplied, but the paraffin oil, light litho varnish, or even the thin dryer added by the pressman was sufficient to cause a puttylike and apparently non-drying condition. Because of such conditions any tests made on an ink which is complained of should be on a sample taken from the fountain, but a sample from the original container should be tested as a check.

Sometimes an ink dries around the edges of the sheet and not in the center. This may be due to the smaller amount of available oxygen in the center, which delays setting of the ink long enough for the varnish to soak in too much. At other times an ink may dry well when printed over another ink, but not when printed directly on the paper. This may be due to the first ink containing a natural dryer, such as chrome yellow or iron blue, which aids the drying of the second ink, but it is more likely that the ink contains too much light-bodied varnish. When such an ink is printed over another, the first has sealed the surface of the sheet sufficiently to hold the second on the surface until it sets, but if the second is printed directly on the paper the varnish soaks in too fast and the pigment does not retain enough to bind properly.

Process printing involves superimposing from one to five or more inks on the paper, and considerable oxygen is necessary to dry them. "Winding," or separating the sheets to admit fresh air and cool the paper, is often necessary when heavy forms are being printed, and if this is not done the heat and lack of oxygen may cause the ink to become soft and sticky rather than dry. As a result the sheets stick together and cause offset, and sometimes the job is completely ruined.

These ink troubles may occur on any paper used in offset printing, while in letterpress work they are usually confined to coated and the more ink-resistant papers. Because of the difference in ink and operating methods they do not occur in the rotogravure process.

A non-drying trouble in offset printing, usually accompanied by curl, occurs when the ink becomes emulsified with water from the fountain etch, either during a long run without a wash-up and ink change, or from the use of an excessive amount of fountain etch. Under the latter conditions offset inks have been found to contain as much as 24 per cent of water after a few hours' press run, but under better conditions the press can be operated much longer before excessive emulsification takes place.

With regard to the drying of an ink, Bekk[1] states that the influence of paper on the chemical changes taking place are at most very minor.

Offsetting is the transfer of ink from the face of one sheet to the back of the next in the pile. It is closely connected with the ink receptivity of the paper, being more in evidence with ink-resistant papers. The condition of the ink and its rate of drying also affect offset; making the ink tackier will accentuate it, as will also any condition tending to retard the drying of the ink. The quantity of ink necessary to maintain the desired color also has an influence; strengthening the color of the ink, and so using less of it, helps reduce offset. The printing of one ink over another sometimes contributes to offset; the first ink should be not quite dry when the second is printed.

Rough handling of the piled sheets and excessive impression on the press make offsetting worse, and electrification of the paper during printing tends to cause the sheets to cling tightly together and thus increase offset. This particular cause of the trouble can be eliminated or greatly reduced by employing an electric neutralizer or by passing the printed sheet over a gas flame. Other cures for offsetting are slip sheets or some of the many non-offset sprays. These are useful in sheet printing, but in web-press operations slip sheets cannot be employed nor can sprays be used with any success between the first and second impressions, because the printing pressure more than overcomes the effect of the offset-preventing material.

Insufficient ink receptivity is an occasional complaint, and the common pressroom remedy is the addition of kerosene, light mineral oil, or light litho varnish. As a result the paper does not take enough ink from the plate, and what is taken off soaks into the paper, resulting in a gray print. The logical remedy is to make the ink tackier, so that more of it will stick to the paper at the instant of impression.

From the paper standpoint ink receptivity in plain papers is very closely associated with the severity of beating of the stock and the amount and nature of the fillers employed. In coated papers the amount of coating, the nature of the pigments, and the kind of adhesive and its ratio to pigment are important factors, and by proper adjust-

ment of these much can be done to control the ink receptivity of the finished paper. In general it may be said that the higher the adhesive-pigment ratio the more slowly the ink is absorbed; no general statement can be made regarding the kind of pigment as this involves a study of each individually. Its importance is shown by tests which proved that of two clays used for coating one permitted the ink to be absorbed in half the time required for the other; similarly of two precipitated chalks one required four times as long as the other for ink absorption.

In addition to the mechanical defects already mentioned, lumps in paper are a fruitful source of complaint. They may be due to any number of causes and are sometimes large enough to injure or ruin the plates. If they are an integral part of the paper they are often traceable to slime growths in pipes or chests, or to strings of fiber which collect on the under sides of screen plates and finally drop off. Lumps may also be caused in coated papers if partly dried coating breaks away from the brushes or any part of the equipment and gets onto the paper before it is dry.

These and many others are the faults of the paper, but there are some which cannot be so definitely placed and which must be looked at very closely in order to fix the responsibility. Lumps which have been blamed on the paper have been found to consist of starchy material resembling cake, apple skins, bits of type metal, lumps of fiber embedded in hard ink, etc. The unreasonableness of some such claims is shown by two which, fortunately, are not entirely characteristic, but were actually made. The first related to a lump which was said to be on the paper when received and which caused a battered plate on a color job. On removal of the lump from the printed sheet the red and yellow half-tone dots were found on the paper under it, while the other colors were on the lump itself. Obviously the first two colors were applied to the paper before the lump appeared on the scene at all. The second complaint was in regard to pieces of wood which were said to have been packed in the case of paper. They were found to be different from any wood used in the paper mill, and as the pieces could be fitted together to make the handle of a make-ready knife it was concluded that the trouble originated in the pressroom. This was later proved to be true.

Scumming or tinting in lithographic printing is caused by the plates picking up a little ink in those areas which should remain entirely free from it. This has at times been attributed to either an acid or an alkaline condition in the paper, but it has not been possible to verify these claims. Another possible reason is the use in the ink of dyes

or lakes which are partly soluble in water and are therefore taken up as light tints by that portion of the plate which has been moistened.

According to Tritton,[7] scumming may be caused if the gum is not first dried on the plate; a more acid gum causes it more quickly than a neutral gum, but the difference is slight. He claims that scum is not formed by an ink of low acid value; with higher acid values, a light scum can be washed off the gum film, but if much ink is allowed to get through the water film the adsorbed gum film will be broken down and a fatty acid film formed. Fatty acids and gums are able to displace each other according to which is present in greater bulk, and if litho inks were free from fatty acids scumming would be unknown.

Complaint is often made that the ink strikes through the paper and causes staining on the other side. This may be true of very fluid inks and light-weight papers, but one ink maker has stated that, with book and coated paper as heavy as $25 \times 38 - 70$, the ink is not made which will strike through. In most such complaints a careful inspection will prove that it is offset rather than strike-through. In those papers where strike-through may actually occur it will be influenced by the type of ink, the temperature of the pressroom, and all those factors affecting ink receptivity, rate of drying, etc.

A trouble sometimes diagnosed as striking through is caused by some material in the ink which causes the print to make a copy of itself on adjoining sheets. At times it is possible to take paper on which the ink is thoroughly dry and make a copy of the print by placing it between white papers and keeping it under pressure for a few days. If this is done at high temperature the copy may appear on several sheets, decreasing in intensity with the distance from the printed specimen. Such copies cannot be attributed to strike-through or offset as usually understood.

Grayness of the cut or filling up of the half-tone are occasionally blamed on the paper, though it is usually a question of improper ink selection or adjustment. Two causes for grayness already mentioned are the removal by the ink of loose particles of filler from the paper and the use of an ink with too little tack to be properly removed from the plate. If the ink is reduced with a liquid, instead of with a less tacky ink, it is also more likely to cause fill-up. Grayness may also be caused by too porous a coating which absorbs so much of the ink that the surface is not well covered. If froth pits in the coating are present in too great numbers, grayness may appear in the print, either locally or generally.

Mottling is a trouble closely related to ink receptivity since anything which causes irregular ink absorption will result in variations in the

printed surface. If such areas of variable ink absorption are large enough to be visible a black solid may show patches of dull and shiny spots instead of a uniform surface of either type. This trouble is distinctly a fault of the paper, and, though its origin is not exactly known, it probably goes back to irregularities in the formation of the paper, or possibly to spotty sizing due to unequal pressure of the web of paper on the drying cylinders. Such variations follow through the coating operation, or may even be made worse by it, so coated papers are even more likely to mottle than uncoated ones.

In half-tones it is said that mottling may be due to filling up of the plate, which causes less ink to be deposited where the dots touch the paper than in the spaces between the dots which should be free from ink.

In color printing where a number of impressions are made, it is of the utmost importance that the colors should register properly. Apart from mechanical troubles in the pressroom the chief cause for poor register is variation in the moisture content of the paper at the time of the different impressions. This is often claimed to be the fault of the paper by printers who believe the paper maker can so treat his product that it will not change dimensions with changing atmospheric conditions. Since there is no known means of doing this, the best that the paper maker can do is to send out his paper with a moisture content equivalent to average pressroom conditions and hope that the paper will print well as delivered or be properly conditioned before printing. The general relations of moisture to printing are discussed in Chapter XVIII.

Smudging or rubbing of the ink on the printed sheet may be a fault of the paper or the ink or both. Inks are made which will not do this, and so are papers, but it is not always possible to combine satisfactory grades of both materials and obtain results which are satisfactory in all other respects. From the paper-making angle smudging is caused chiefly by certain more or less abrasive pigments such as the blanc fixe used in the coating, and if these can be avoided smudging will be eliminated or greatly reduced.

Experiments on Printing. The building of specifications for paper has necessitated studies of the properties of the papers and their correlation with the printing results. This has resulted in the accumulation of much information which does not fit into the foregoing story, but which is nevertheless of value to one who is making a careful study of the problem.

A very interesting paper by Prior[6] describes a hand-driven proofing press and numerous studies made with it. The maximum speed of this press was 200 feet per minute while the speed of bed movement in com-

mercial presses was said to be from 120 to 1000 feet. With hard packing and with a " kiss " impression the pressure applied to the paper may be as much as several hundred pounds per square inch. By inserting a thin lead foil under the paper the degree of embossing can be shown; the lead foil does not spring back on releasing pressure, while the paper does to some extent.

An interesting feature of this study was the use of a microscope slide as a solid plate to print from. By weighing this after inking and after impression, the film of ink removed by the paper could be determined, and the nature of the ink distribution could also be studied. From this work the data of Table 75 were obtained.

TABLE 75

	Normal Thickness of Film		
	Before Printing	After Printing	Per Cent Transferred
	μ	μ	
News ink and paper.......	2.1	1.0	52
Art ink; coated paper.....	2.4	0.6	75
Short ink; newsprint......	2.1	1.1	40

The ink distribution was found to be more or less irregular or reticulated, according to the ink used, a condition which is often noticed in papers printed with tints as a base or background.

With regard to offset, Prior does not believe that oil-absorption tests prove anything, and he doubts that absorption of oil vehicle, thixotropic loss of fluidity, or formation of a skin by oxidation can be rapid enough to prevent it.

Bekk[1] has described a number of instruments that measure the properties of paper which he thinks have an important influence on printing. He considers smoothness one of the most important points in regard to transfer of ink, and this smoothness must include that caused by the printing pressure. This brings in the factors of softness, embossing, etc., and it is pointed out that surface softness is not the same as total sheet softness, for printing pressures do not compress the sheet uniformly throughout. Softness of the body of the paper is important in regard to print transfer, as it enables any irregularities in plate or paper thickness to be equalized. It is obvious that the rougher the paper surface the greater the pressure necessary to give complete ink transfer, which brings in the question of the squeezing out of the ink. The size of the dots in a half-tone determines the reproduction of tones, and their con-

tour controls the finer details. If the pressure squeezes out the ink, its distribution on the paper will not be the same as that on the plate and detail will be lost. This is less serious on smooth than on rough papers, because the smooth change the area of the ink more than the contour of the dots.

Ink also influences this squeezing out, or skid, as the thinner the layer applied the more it will resist displacement. High-viscosity ink also gives less skid, but this is limited by the nature of the paper. High ink receptivity is another aid in reducing ink skid. This factor is of considerable importance in rotogravure paper as the pressure of the rubber-covered roll forces the paper into the depressions of the plate and the ink is thus forced into the paper.

According to Larocque[4] the resistance of paper to oil is a direct measure of its ease of penetration by printing ink, and hence is related to such troubles as offset, strike-through, rub-off, and lack of gloss. He found the influence of temperature on oil absorption to be about 9 per cent per degree centigrade, and with six different oils the absorption time was proportional to the quotient " oil viscosity/surface tension " of the oil. His experiments indicated that the structure of the sheet could not be assumed to be a uniform capillary system throughout, but that there was a surface layer which was considerably more oil resistant than a layer of equal thickness in the interior of the sheet. For equal bulk the sheet having the more finely divided material was the more oil resistant, and beating and calendering increased oil resistance more than wet pressing. The presence of 2 per cent of rosin size, on the other hand, increased wettability by oil by about 25 per cent.

In another article the same author[5] states that the amount of ink transferred to the paper increases with the printing pressure, the smoothness of the sheet, and its softness. He found the amount of offset to vary directly with the surface oil resistance and inversely as the smoothness of the paper.

Rating Half-Tone Prints. This may be done by selecting as standards for comparison a set of prints from the same plate, but of varying smoothness and uniformity, from the highest possible quality to one which is quite unsatisfactory. Comparison of prints from the same plate with these standards will give valuable information, provided papers of the same class are considered, and the system can be extended by selecting standards for the different grades of papers.

Studies of this nature on coated papers have shown that the microscopic appearance of the surface may vary greatly without changing the rating of the printing. A high printing rating may be had with much ink skid on the half-tone dots or with almost none. The amount of

ink skid varies with the kind of pigment, with its particle size, and with the kind and amount of adhesive in the coating mixture. Considering the regularity of dot contour and ink distribution, the order of importance for high printing rating seems to be about as follows:

1. Even dot contour, plus perfectly even ink distribution.
2. Even dot contour, though accompanied by much ink skid.
3. Poor dot contour, plus even ink distribution.
4. Poor dot contour and ink distribution.

On glossy coated papers the use of little ink tends to roughen the dot contour slightly, while with more ink the contour is better because so much is squeezed out to the edge of the dot that it automatically becomes smooth. The chief area within the dot is gray in either case because the ink either was not deposited or has squeezed out. If froth pits are present in the coating they tend to break up the dot contour and lower the printing rating.

Varnishing. The varnishing of paper to increase its suitability for special purposes involves the application over both printed and unprinted portions. Two types of varnish are used, a " spot varnish " which is practically a colorless printing ink and is handled on the press in the same way, and a " spirit varnish " which is not applied on a press but is usually handled in a separate plant which specializes in such work. The machine used is somewhat similar to the fountain end of a cylinder press; after the sheets are varnished they go through a heated chamber to drive off the solvent, and can then be piled without sticking.

Little difficulty is experienced with either type of varnish when applied over printed areas, but on the unprinted parts lack of gloss, loss of opacity, and change in color are causes for complaint. Spot varnish is likely to be worse than spirit varnish.

Many factors affect varnishing, but as yet little intensive study has been given to the problem. It is known that spirit varnishing is greatly influenced by the kind and amount of the adhesive used in the coating, as well as the kind of pigment. The drying temperature of the coating is also of importance, as too high a temperature may spoil the varnishing even though pigments and adhesives were right for normal drying temperatures. In some such cases the gloss obtained was satisfactory but the loss of opacity was excessive.

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CHAPTER XVIII

MOISTURE RELATIONS OF PULP AND PAPER

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This chapter is an attempt to assemble a few of the more important facts regarding the relation of moisture to pulp and paper. Since the manufacturing processes for both are carried out in the presence of water, or are influenced by its presence, or that of water vapor, and since the satisfactory use of paper by the consumer often depends on the proper adjustment of its moisture content, it is obvious that a full understanding of the subject is of extreme importance. The problem is one of great complexity, as it includes temperatures all the way from those in the pulp digester to room temperatures or lower, as well as all ratios of fiber to water from about 1 to 200 up to about 98 to 2. Some of the products made demand extreme resistance to both water and water-vapor penetration, while others must be very absorptive in order to be of service. It is, therefore, quite hopeless to attempt a comprehensive treatment of the subject in one short chapter, but because of its importance attention must be called to some of the facts and problems.

Pulp Making. The present pulp-making processes are all wet processes — cooking, washing, screening, bleaching — up to the time the pulp goes over the dryer to be baled for shipment. When the pulp is used in the same plant in which it is produced this final drying is usually omitted and the pulp is delivered to the beaters in the wet state. It is generally acknowledged that fibers which have been kept continuously wet act quite differently in the beater from those which have been dried, and for certain types of paper undried fibers are quite essential. This difference between wet and dry fibers is well brought out in the following table, which gives the bursting strength for sheets of the same fiber which had been given the same amount of beating, but which had been slowly and carefully dried to different degrees before beating:

MOISTURE IN PULP BEFORE BEATING	BURSTING STRENGTH POUNDS PER SQUARE INCH
70	64.7
60	60.8
50	59.0
40	57.7
30	56.4
20	54.0
10	48.8
5	39.5
0	11.0

One might assume from this that the wet pulp is in a plastic state which allows strength to develop rapidly on beating, and that on drying this is gradually altered to a condition which considerably retards strength development. It appears to be very largely an irreversible colloidal change, for subsequent soaking in water restores its original condition to only a slight degree.

In support of this theory, it has recently been stated by Weidner[38] that unbleached sulfite pulps which have been brought to equilibrium with an atmosphere of 95 per cent relative humidity, without passing through a drier state, contain 38.8 to 41.1 per cent of moisture, but that after they have been dried and again brought to equilibrium with the same atmospheric conditions their moisture content is only 23.3 to 24.4 per cent. A difference such as this is almost certain to influence the paper-making behavior of the pulp.

The change of strength cited above for sulfite pulp is most certainly due to moisture variations, but whether similar changes would be shown by sulfate and soda pulps during the drying-out process is not yet known. It also suggests that wood which has been kept wet from the time of cutting until it is cooked may produce quite different pulp from that prepared from thoroughly dry and seasoned wood. This is apparently true for groundwood, for Maass and Campbell[18] say that it does not seem possible to make quite the same quality from wood which has never been dried and that which has been dried below its saturation point and then resoaked.

Beating. Any discussion of beating brings up such terms as "freeness," "slowness," "greasiness," "wetness," and "hydration," most of which were coined to describe an obvious quality in the pulp caused by beating operations. "Hydration," however, seems a particularly unfortunate selection, because its association with definite chemical changes in other lines of work has led to similar assumptions in respect to fibers.

Paper makers' " wetness " or " hydration " is evidenced in the beaten stock by a soft, slippery, slimy feel, a greater power to retain water (resistance to drainage), and more tendency to slide on the cylinder molds and to crush under the dandy roll or on the presses. In the paper it is shown by greater shrinkage, translucency, hardness, and density. The properties of wetness are induced by beating, and various types of freeness or slowness testers have been developed to measure the degree of such treatment. Since their indications may be influenced by shortness of fiber as well as the amount of its hydration, it is apparent that the same reading may be given by a highly hydrated, long fiber or a short fiber of low hydration, and that such instruments measure only the total results of beating.

To obtain an actual measurement of " hydration " proper, Le Compte[16] made use of a method devised by Guild and Mills.[8] This consists in measuring the wetness of the stock before and after boiling in water for an hour, and cooling. Boiling destroys the slowness due to hydration, but not that due to shortness of fiber, so the difference in the two readings is a measure of the hydration. In developing this method it was found that the slowness after boiling remained constant for several days, but over a period of several months it gradually increased until all the slowness due to hydration was regained. By vigorous agitation with a motor stirrer the recovery of slowness was complete in about 35 minutes. This apparently disagrees with the theory that cellulose has the characteristics of an irreversible colloid, but possibly the original plastic condition and the hydration due to beating are not the same.

The question of whether hydration is an actual taking up of water to form definite chemical compounds has received much attention, and though the theory has not been abandoned by all, the general conclusion is that the changes caused by beating are of a physical nature. Strachan[32] finds no evidence of a definite vapor pressure, as would be expected in a true hydrate; the dehydration curves were unbroken, indicating a continuously variable vapor pressure, and hence physically held water. He found the vapor pressure of the last traces of water very low and its boiling point high, so that it was impossible to remove it completely at 100° C. Russell, Maass, and Campbell[28] measured the sorption of beaten and unbeaten kraft and unbleached and bleached sulfites at relative humidities ranging from 0 to 100 per cent and found that beating made practically no difference and hence caused no change in the hydration of the cellulose. Seborg and Stamm[30] studied the relation of moisture content to relative humidity and electrical conductivity and found the hygroscopicity of the pulp un-

affected by beating, but in a later paper Seborg, Simmonds, and Baird[31] state that by extreme beating the hygroscopicity of the pulp is definitely increased by about 6 per cent of the moisture content of the original pulp. McGregor[20] experimented by freezing-point methods, by rate of drying over sulfuric acid, and by displacement methods with ethyl alcohol, and concluded that water is not bound by the fibers during beating but remains in the free state.

Considering other possible chemical changes during beating Strachan states that organic analysis for carbon, hydrogen, and oxygen shows no difference between natural cellulose and that highly hydrated. Curran, Simmonds, and Chang[4] claim that the chemical constitution of stuff beaten 4–6 hours in an approximately neutral aqueous suspension was the same as that of the unbeaten pulp. Kress and Bialkowsky[14] find that the alpha-cellulose, copper number, and soda solubility of unbleached Mitscherlich sulfite pulp remain practically unchanged during a beating so severe that the final stock would have been unsuitable for machine operation.

Campbell[1] concludes that when fibers are immersed in water it is adsorbed on every exposed crystal surface and a layer of hydrated cellulose is thus formed. This lowers the attraction of the crystallites for each other and allows more water to enter, thus causing further imbibition and swelling. Beating causes stressing and bending of the swollen fibers, makes them more flexible, and fibrillates them with the production of a much greater external surface.

After careful reading of the literature relating to beating and hydration one is left with the feeling that the various theories to account for the union of water with cellulose have been put forth by individuals who have been so close to their own work that they have failed to realize that a number of actions may be taking place simultaneously. It is easily possible that the mucilage formation of Schwalbe, the fibrillation of Strachan, and the crystallite hydration of Campbell may all play a part and that the effect of each may be so obscured by the others that it is not possible to determine their individual magnitude or importance. There is also the possibility that any one of these may cause physical changes which are entirely out of line with its apparent importance as judged by chemical means. The various theories seem to form a more or less closed circle, and the wise reader would do well to focus his attention on the things which can be shown to influence definitely the character and strength of beaten pulps. An excellent summary of present theories of hydration and an attempt to bring them together into a simple composite theory is given by Clark.[3]

Kress and Bialkowsky[14] report on work in which they studied the effect of beating unbleached Mitscherlich sulfite in a number of liquids besides water and compared these results with those for swelling as measured in a dilatometer.   They found that when beaten in fuel oil, butyl alcohol, amyl alcohol, amyl chloride, and furfural the fibers were cut sharply, with no fibrillation, and when freed from the medium in which they were beaten and made into sheets from water they showed very little strength and no grease or water resistance.   The same fiber when beaten in ethylene glycol, methyl alcohol, and form-amide showed good fibrillation and gave sheets very similar to those from stock beaten in water.   The dilatometer proved that the liquids which permitted little development of strength on beating caused very little swelling of the fibers, while those which permitted strength to develop also caused much swelling.   From this work it appears that liquids of low dielectric constant do not have swelling or hydrating capacity, while those with a high dielectric constant and a hydroxyl or potential hydroxyl group do permit both swelling and hydration.

Somewhat similar work was carried out by Edge,[5] who beat fibers in toluene, filtered and air-dried them, and then soaked them in water over night.   He then opened them up slightly in a disintegrator and made them into sheets.   Although the fibers were more highly fibril-lated than those beaten in water the sheets made from them were very much weaker.

Young and Rowland[39] carried the work with the dilatometer a step further and proved that with softwood pulps the swellability increased with the pentosan content in an approximately linear manner.   This seems to indicate a close relationship between pentosan content and hydrating capacity in the beaters.

Strachan[32] has investigated the absorption of water by fibers, which he terms "imbibition," using vulcanized fiber as the basis of his work.   He defines imbibition as the "process of drinking up water like a sponge after atmospheric adsorption has reached a maximum," and considers its chief characteristic to be a swelling of the material as it takes up water.   The rate of imbibition was rapid at first, but it then slowed down and continued for a long period of time.   During the period when swelling did not occur the rate of imbibition was proportional to the specific external surface, but after swelling came into play the rate increased greatly.   Imbibition increases with pres-sure and also with reduced pressure, which removes air from the fibers and increases the surface exposed to water.   High temperature of the water was found to increase the rate of imbibition because of removal of air, but if the fiber is thoroughly saturated with water its percentage

of water of imbibition drops with rising temperature, especially above 40° C. He concludes that the immense surface created by fibrillation, plus the pressure exerted, is sufficient to account for the increased imbibition generally called " hydration."

In a later paper Strachan[33] claims to have found that after washing the usual impurities out of cellulose the cellulose continues to dissolve in definite amount in repeated extractions. The solubility is said to be about 20 mg. per liter of water. As the determination was made on pulp which was stirred at 5 per cent density for 2 hours there seems to be a possibility that the " dissolved " cellulose might consist of particles worn off the fiber mechanically and present in colloidal suspension. In the same paper he refers to the former theory of fibrillation, not as a splitting of the fibers, but as raising a sort of " pile " on its surface.

Harrison[10] believes that the strength of paper made from wood pulp is almost independent of fibrillation, which he considers merely incidental as far as Hollander beating is concerned. He considers that the main changes are imbibition and a change in the fiber surface promoted by pressure. He thinks that the greater pliability of the beaten fibers gives greater areas of contact and hence greater strength. This would seem to be another form of Strachan's fibrillation theory, except that the fibrillation may be so fine as to be invisible under the magnification which is usually employed in microscopic examinations.

Edge[6] does not consider wetness and hydration synonymous. The capacity to develop wetness may be due to the presence of parenchyma or similar cells, or to non-cellulose matter. He considers the formation of pulp mucilage an important factor in strength development.

Regarding the temperature of beating Lewis and Gilbertson[17] find that the time required to reach a given freeness is somewhat less at 25° than at either 6° or 45° C., and that it is greater still at 80° C. They also confirm the previous statement that the chemical constants — alpha-cellulose, copper number, and cuprammonium viscosity — are not affected by the time or temperature of beating. Hall[9] also finds that temperature does not affect the nature of the beating, but only its speed. If the stock is beaten to the same slowness, hot or cold, the same strength is found in the sheets.

Practical Aspects of Beating. Because all beating operations involve the relation of fibers and water, mention may be permitted here of some of the facts and fancies relating to beating.

It is often claimed that stock which has been left in chests or drainers for some time, as over a week end, will work up " wetter "

than freshly prepared stock. This statement is so persistent that it seems as though it must have some basis in fact, but an attempt to verify it by tests of bleached soda poplar fiber which was held in a drainer for 30 days failed to show any significant differences. Possibly cotton and linen may respond to storage conditions to a greater degree than wood fibers, or perhaps changes are evident in paper-machine operation which cannot be detected by laboratory methods.

Different types of fiber are known to act very differently when beaten. Kraft sulfate develops considerable bursting and folding strength long before any splitting, shortening, or fibrillation shows under the microscope, or before any appreciable slowness or wetness is shown by the usual tests. It is also common knowledge that purification of cellulose, as in the preparation of so-called alpha-cellulose, greatly decreases its ability to become slow or wet. The different kinds of sulfite, as Mitscherlich and ordinary quick cook, behave very differently in the beater, and the proper selection must be made for paper of any given type. Strachan claims that it is impossible to " hydrate " overbleached stock, but Obermanns[25] says that an increase in hemicellulose decreases the time required to beat to a given slowness, and that this holds for pulps degraded chemically as well as for those to which hemicellulose fractions are added.

Besides the nature of the fibrous materials, the condition under which they are beaten must be considered. Dissolved substances may be present in the beater and may affect the results by their specific action or by rendering the material acid or alkaline. It is claimed that sulfite cellulose fibrillates more easily in an alkaline than in an acid medium, but that good formation on the wire is more difficult to accomplish with an alkaline furnish. The presence of filler also influences the development of strength to a marked degree, and there is some evidence that fiber and filler beaten together give greater bursting and folding strengths than if an equal quantity of filler is added after the beating.

Formation, Pressing, and Drying. These are all operations in which water is removed from the paper stock in one way or another. About all that can be said of sheet formation at the present time is that it is greatly affected by the water-fiber ratio as well as by the characteristics imparted to the stock by beating. Very little attention has been given to water at the paper machine, except to use as little as possible for the sake of economy, but it is beginning to be realized that formation may be considerably influenced by the pH of the water and by the presence of very small amounts of substances, largely of a colloidal nature, which are either added intentionally or formed

during the treatment of the stock. Much more study should be given to this phase of paper making.

Pressing for the removal of more water than can be taken out on the wire or at the suction boxes need be mentioned only in passing. It is considered almost wholly a mechanical operation, which may or may not be true.

Drying has always been given much attention because of the cost of the operation and its effect on the speed of the paper machine. Nearly all the studies have been devoted to increasing the efficiency of the process or equipment, and relatively little attention has been paid to the effects of changing water-fiber ratios. That this may influence the characteristics of the paper to a considerable extent is realized by Clark,[2] who states that a bond paper which has been overdried at any time during its course of manufacture has lost very definitely in folding, tearing, and tensile strengths, its surface is less absorbent to printing ink, it is more difficult to calender to a definite standard of finish, and it is more sensitive to changes in relative humidity and more likely to curl.

Rasmussen[26] believes paper should leave the dryers with as high a moisture content as possible, which for newsprint may be as high as 9 per cent. As to rate of drying he cites the work done by several sections of a dryer bank under two different systems as follows:

	SYSTEM 1	SYSTEM 2
First quarter of dryers	39%	23%
Second quarter of dryers	29%	27%
Third quarter of dryers	22%	27%
Fourth quarter of dryers	10%	23%

Whether either of these procedures gave the best possible paper from the stock available was entirely a matter of conjecture.

Minton[23] recognizes some of the problems of paper quality as related to drying and believes that each kind of paper has a different requirement for critical temperature of drying in order to bring out the characteristics desired. He states that pulp dried to 91.8 per cent bone dry at high temperature loses strength, but that if it is dried to the same degree at 100° F. in a vacuum it does not. In discussing newsprint dried in a Minton vacuum dryer, Gough and Hill[7] state that as compared with paper dried at atmospheric pressure it is softer, brighter, more porous, more absorbent to oil and water, slightly more bulky, and a little lower in bursting strength.

Calendering. It is well recognized that the moisture in the paper when calendering has a great influence on the character of the paper obtained. Increased moisture means that, for a definite finish, less

weight can be applied to the calender stack, or it can be run at lower temperature. If a higher finish is desired, greater moisture necessitates a lower stack temperature in order to avoid blackening, or " burning." This appearance is not caused by overheating, but is due to small translucent areas in the paper which reflect much less light and hence appear dark. These are much worse in damp paper because it is so much more plastic that the thicker spots are easily crushed at the pressures used in calendering.

The difference in calendering conditions necessitated by variation in the moisture in the paper is shown by the following approximate data:

GLOSS OBTAINED	PAPER MOISTURE	CALENDER TEMPERATURE	WEIGHTS ON STACK
30	3.5	170	5
30	6.0	150	3.5-4
40	6.0	150	Still less.

Strachan[32] considers that the momentary high pressure on the calenders, equivalent to 10,000–20,000 pounds per square inch, produces hydration and fusion of the plastic cellulose. He finds that ordinary calendering increases strength about 5 per cent, but in water finishing it may be as much as 20 per cent. Imitation greaseproof has been made by running a fine, free stock through the calenders in a damp condition.

Moisture in Paper. The fact that paper becomes limp on a damp day and stiff and rattly on a dry one has probably been known since paper has been made, but Herzberg[11] and Klemm[13] appear to have been among the first to make any definite study of the subject. Since that time many data showing the influence of atmospheric humidity on the moisture content of paper and on its strength and various uses have been collected.

Kress and McNaughton[15] studied the moisture content of about 25 papers of approximately known fiber furnish and of very different grades, and found that it varied directly as the moisture in the air, though it was also found that at a given relative humidity different papers contained different amounts of moisture. It was impossible to establish any definite relation between type of furnish and moisture content. McKee and Shotwell[21] found that the moisture content of paper varied with the absolute humidity for temperatures between 60° and 110° F. If the relative humidity was kept constant a decrease in temperature below 60° F., or an increase in temperature above that point, increased the moisture content of the paper.

In the early work ' along this line unexplainable variations were sometimes encountered, and it now seems highly probable that these were due in part to the fact that equilibrium was approached indiscriminately from a drier or wetter state. More recently it has become generally accepted that there is a hysteresis effect in moisture absorption, so that for a given humidity a paper will contain more moisture if it approaches equilibrium from a wetter condition than it will if it comes to equilibrium from the dry side. Characteristic hysteresis curves are shown in Fig. 7. Because of this inherent property of cellulose and the variations caused by beating, bleaching, and fiber furnish, it is impossible to construct a table or curve from which to calculate the moisture content of any paper under any of the normal conditions of temperature and humidity, but in general the changes follow the type of curve in Fig. 7.

Merely as characteristic examples the data of Table 76 are presented.[22] (See page 508.)

Among others, Seborg, Simmonds, and Baird[31] studied the hysteresis effect and found it to persist undiminished through seven complete cycles from dryness to 95 per cent relative humidity and back. The final ratio of absorption to desorption moisture was from 0.85 to 0.88 for a variety of chemical wood pulps and stuffs, and for wood pulps was approximately constant regardless of species, amount of spring or summer wood, pulping process, degree of beating, or degree of bleaching. For sulfuric acid lignin and cuprammonium lignin the hysteresis ratios were 0.78 and 0.79, respectively.

Repeated wetting and drying of western hemlock sulfite showed a decreasing moisture content for each desorption curve up to the sixth cycle, but no change thereafter. This shows only in the range between 93 and 50 per cent relative humidity; below 50 per cent the curves coincide. This reduction in hygroscopicity was the same for bleached and unbleached pulps; it seems to be strictly related to cellulose. The adsorption moisture relations of this pulp appeared to be independent of the effects of alternate soaking and drying; the original and final adsorption curves coincide.

Weidner[38] has made some very interesting studies of single fibers of sulfite spruce pulp and finds that, after the first desorption, hysteresis in fiber diameter persists unchanged. This checks for dimensional changes, the observations of Seborg, Simmonds, and Baird for moisture content, and would seem to tie up moisture and expansion changes of papers with those of individual fibers. In the course of this work Weidner observed a change in the appearance of the fibers during desiccation. The wet fibers were transparent, but as desorption

TABLE 76

MOISTURE CONTENT OF PAPER FOR AIR AT

Relative humidity	47%	65%	81%	87%	95%
Temperature, ° F.	78	76	75	78	84
Grains per cubic foot	4.83	6.28	8.07	8.94	11.75
Paper					
A..............	4.55	6.2	7.95	10.35	16.45
B..............	4.9	6.65	8.5	10.75	15.95
C..............	4.5	6.1	7.7	9.6	14.4
D..............	5.7	7.15	9.3	11.35	16.9
E..............	8.55	10.65	12.5	16.2	21.3

The first four samples were book papers and the last a newsprint; moisture percentages are on the bone-dry papers.

MOISTURE CONTENT OF CELLULOSIC MATERIALS AT

Absolute humidity grains per cubic foot	1.49	2.99	4.98	6.97	8.97
Material	%	%	%	%	%
Cotton cloth...........	2.99	4.56	6.7	9.7	13.5
Linen cloth............	2.53	5.60	5.1	7.0	10.2
Jute (average).........	4.33	6.9	10.2	14.4	20.2
Sisal hemp rope........	4.48	5.6	8.3	11.7	15.1
Manila hemp...........	4.25	5.6	8.5	11.7	16.0
White viscose..........	5.6	6.7	9.4	12.9	16.8
Red viscose............	5.3	6.4	9.0	11.8	15.2
Mechanical pulp........	4.55	6.3	7.9	9.5	12.0
Soda pulp, unbleached..	3.49	5.0	6.6	8.0	10.2
Kraft paper............	2.50	3.85	5.4	7.0	9.2
Bond paper............	2.54	3.71	5.1	6.5	8.1

VARIATION OF MOISTURE CONTENT WITH TEMPERATURE

Newsprint at constant absolute humidity of 5 gr./cu. ft.

Temperature, ° F.	Moisture Content, Per Cent
40	10.0
50	8.8
60	8.2
70	8.1
80	8.15
90	8.1
100	8.0
105	7.0

Offset at constant absolute humidity of 7.25 gr./cu. ft.

76	7.25
86	8.32
94	7.20
104	3.57

proceeded they became more opaque; on adsorption they again became transparent. The most noticeable changes were between 0 and 12 per cent and between 58 and 95 per cent relative humidity.

This work shows a definite connection between fiber dimensions and the relative humidity of the surrounding air, over the range of 0 to 95 per cent, and at 25° C. From 0 to 36 per cent relative humidity and from 0 to 5–7 per cent moisture content the correlation between moisture content and fiber diameter is very good; from 36 to 60 per cent relative humidity it is fair, but above 60 per cent there seems to be no correlation. The first desorption changed the length of the fibers of three sulfite pulps 1.5 to 1.6 per cent and their widths 9.0 to 9.6 per cent. On subsequent adsorption and desorption the total changes were 0.8 per cent in length and 7.4 to 8.3 per cent in width.

The effect of moisture in paper on its strength and physical properties is far reaching and of great importance to most of its users. It makes it necessary to test for strength, under conditions of constant humidity and temperature, for if this is not done, papers which are made according to specifications but tested at the wrong humidity, may prove to be unacceptable when correctly tested, thus leading to very considerable losses. Unfortunately a paper mill's customers are often so scattered geographically that it is not possible to turn out a product which will be in equilibrium with all the climatic conditions represented, so the best that can be done is to maintain as nearly an average condition as possible. Even this is not a simple matter for the average summer condition is not the same as that in winter and a plant located at seaboard will be quite different from one located inland and away from any large body of water. The average relative humidity indoors is said by Reed[27] to be not over 40 per cent, while in another plant in a different part of the country it was found to be between 49 and 50 per cent. A general survey of twenty or more printing plants showed considerable variations in humidity, but the average was between 50 and 55 per cent.

A considerable number of articles relating to the effect of humidity on the strength of papers have been published, and Reed has shown that the folding strength is affected by both humidity and temperature, but not to the same extent in all papers. Houston, Carson, and Kirkwood[12] made a careful study of eleven papers at humidities ranging from 15 to 83 per cent and also found considerable variation between samples. Their average results are shown in Fig. 50 on page 448. The variation between samples is not surprising, considering the effect of beating on hygroscopicity as shown by Seborg, Simmonds, and

Baird, and their claim that it is also affected by bleaching. Hysteresis may also be responsible for some of these differences.

The bursting strength of container boards was found by Seborg, Doughty, and Baird[29] to be at a maximum at about 40 per cent relative humidity on adsorption and at 30 per cent on desorption. Between 25 and 65 per cent relative humidity it dropped from the maximum figure by only about 5 per cent, but outside of this range the loss became serious. Morgan and Kress[24] studied the effect of hysteresis in moisture content on the physical properties of paper and show in Table 77 the percentage differences when tested at 65 per cent on the desorption side as compared with tests at 65 per cent on the adsorption side. Eighteen papers were tested.

TABLE 77

Property Tested	Percentage Difference	
	Maximum	Average
Basis weight..............................	+2.7	+1.84
Bursting strength...........	−29.3	−4.90
Tensile strength, with......................	−13.3	−5.76
across................................	−12.1+18.2	−6.51
Stretch, with.............................	+32.3	+14.40
across................................	+50.8	+12.76
Tearing strength, with.....................	+15.0	+3.42
across................................	+14.6	+2.32
Expansion, with..........................	+0.14	0
across................................	+0.38	0.08

Moisture vs. Printing. Of an importance greater than the actual moisture content of a paper is the rate at which it will change when transferred from one relative humidity to another. This will vary with the difference between the first moisture content of the paper and that which it would have at the humidity to which it is moved, and McKee and Shotwell[21] state that it may reach as high a rate as 1.75 per cent per second. The initial rate is high, but it slows down as the paper approaches equilibrium, which it may reach in $2\frac{1}{2}$ hours or more if suspended in single sheets where air circulation is good. In a later report the same authors[22] find that if jets of air impinge on the surface of the paper the rate of moisture regain may be as high as 3 per cent per second.

These figures are for single sheets, thoroughly exposed to the air, and represent ideal conditions which are almost never met with during the use of paper. In printing plants it is much more common to use

paper from piles in which the edges and upper sheet are exposed, while the inside of the pile is well protected. Under such conditions the absorption of moisture downward from the top of the pile is much slower than might be expected. In one case where the paper was moved from a relative humidity of 20 per cent to one of about 71 per cent at 52° F., and exposed without moving for 2 hours, the three upper sheets gave the following weight records:

	ACTUAL WEIGHT	THEORETICAL WEIGHT AT EQUILIBRIUM	DEFICIENCY IN REGAIN
	Grams	Grams	Grams
Top sheet	82.6	83.1	0.5
Second sheet	82.1	82.9	0.8
Third sheet	82.5	84.0	1.5

This very slow penetration of moisture makes it impossible to season paper in piles within any reasonable time, and explains the difficulty in avoiding wrinkled edges when the sides of a pile of paper are exposed to variations in humidity.

Since good register in jobs in which the paper has to pass over the press several times depends on the sheet's retaining its exact size and shape, the interest of the printer in humidity and moisture in paper is easily understood. It is frequently attempted to overcome misregister by seasoning the paper before use, to insure its coming to equilibrium with the atmosphere of the pressroom. Very often this is not entirely successful because sufficient time and exposure are not allowed for the change in moisture to take place and because moisture hysteresis has not been taken into account. Weber and Geib[37] have shown that papers conditioned to pressroom conditions in the usual way continue to expand during the first few printings and give poor register. If the paper was first conditioned at very high humidity and then at that of the pressroom very satisfactory results were obtained, and the same effect was produced by conditioning in the usual way at a relative humidity of 5 to 8 per cent above that of the pressroom. In this work all dimensional changes during printing were accounted for by changes in moisture content, and no evidence of mechanical stretch was found.

Regarding register troubles McKee and Shotwell[21] make the statement that paper absorbs moisture more speedily than it discharges it, and that, though absorption and stretching occur rapidly enough to cause misregister, loss of moisture and shrinkage seldom do. Weber and Cobb[36] believe that the amount of water used on an offset press is unimportant from the standpoint of register, as doubling the amount

used had no serious immediate effect. Weber[35] has demonstrated that for papers made of chemical wood pulps the best register is given by those in which the fibers have the least beating and which, therefore. have the most pronounced difference in crosswise and with-grain directions. This did not hold true for all-rag papers.

Waterproofing. The paper maker's problems in regard to paper and moisture also include those relating to the manufacture of products which are impermeable to water or water vapor, which are quite different things. There are many ways for accomplishing these ends, as is evidenced by Matagrin's monograph[19] on the subject, which includes 791 references. Wandrowsky[34] states that there are three general methods for waterproofing paper: (1) impregnating with a water-resistant material, (2) surfacing with a resistant coating, and (3) impregnating or treating the separate fibers before forming the sheet. The last method includes treatment with such materials as aluminum acetate and aluminum soaps, which make the paper waterproof but not resistant to passage of water vapor.

Papers of this sort are of great and growing importance in packaging goods, and much attention is being given to the requirements for each particular line, and to the methods for testing the product for suitability. The paper maker himself makes extensive use of waterproof wrappers in packing paper in cases and in covering that shipped in rolls. Though affording ample protection in general they cannot absolutely prevent the penetration of moisture but can retard it tremendously.

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INDEX

515