The Institute of Paper Chemistry

Appleton, Wisconsin

Doctor's Dissertation

The Papermaking Properties of Highly Purified Pulps

by T. Richard Probst

June, 1939

THE PAPERMAKING PROPERTIES OF HIGHLY PURIFIED PULPS

A thesis submitted by

T. Richard Probst

B.S. 1935 The Pennsylvania State College
M.S. 1937 Lawrence College

in partial fulfillment of the requirements of
The Institute of Paper Chemistry
for the degree of Doctor of Philosophy, from
Lawrence College, Appleton, Wisconsin

June, 1939

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INSTITUTE OF PAPER CHEMISTRY
Appleton, Wisconsin

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TABLE OF CONTENTS

		Page
I.	STATEMENT OF PROBLEM	1
II.	HISTORICAL SURVEY	2
	A. PULP PURIFICATION	2
	B. THE ACTION OF ALKALIES ON CELLULOSE	5
	C. FIBER STRUCTURE	9
	D. BEATING	12
	E. SORPTION OF WATER VAPOR	16
	F. OPTICAL PROPERTIES	18
III.	MATERIALS AND METHODS	21
	A. PULPS USED	21
	B. PREPARATION OF SAMPLES	21
	1. The Hot Process	21
	2. The Cold Process	23
	C. CHEMICAL EVALUATION OF THE PREPARED SAMPLES	23
	D. BEATING CHARACTERISTICS OF THE WOOD PULPS	24
	E. BEATING CHARACTERISTICS OF THE RAG STOCKS	25
	F. SWELLING CHARACTERISTICS OF THE SAMPLES	25
	1. Cuprammonium Swelling	25
	2. Swelling in 17.5 Per Cent Sodium Hydroxide	27
	G. DETERMINATION OF FACTORS CAUSING INCREASED OPACITY OF PULPS	28
	H. EQUILIBRIUM MOISTURE OF SHEETS	28
	I. EFFECT OF RELATIVE HUMIDITY ON FIBER WIDTH	28
	J. CAPILLARY RISE IN SHEETS	30

TABLE OF CONTENTS (Continued) Page

IV. RESULTS AND DISCUSSION OF RESULTS 32

A. YIELD AND CHEMICAL CONSTANTS OF THE PREPARED PULPS. 32

B. BEATING CHARACTERISTICS OF THE WOOD PULPS 34

C. THE RELATION BETWEEN THE PHYSICAL CHARACTERISTICS AND CHEMICAL COMPONENTS OF PURIFIED PULPS 50

D. BEATING CHARACTERISTICS OF RAG STOCKS 52

E. CUPRAMMONIUM SWELLING 55

F. SWELLING BEHAVIOR IN 17.5 PER CENT SODIUM HYDROXIDE 57

G. OPTICAL PROPERTIES. 60

H. EQUILIBRIUM MOISTURE OF HANDSHEETS. 67

I. EFFECT OF RELATIVE HUMIDITY ON FIBER WIDTH. 69

J. EFFECTIVE CAPILLARY SIZE OF HANDSHEETS. 72

K. MULTISTAGE COOKING. 76

L. PHOTOMICROGRAPHS OF BEATEN AND UNBEATEN STOCK . . . 79

M. ATTEMPTS TO DEVELOP PROPERTIES IN MERCERIZED PULPS. 91

V. CONCLUSIONS 94

VI. LITERATURE CITED. 97

LIST OF FIGURES

Figure		Page
1.	Rate of Development of Original and Alpha-treated Sulfite.	37
2.	Rate of Development of Original and Alpha-treated Kraft. .	38
3.	Mullen Development of Original and Alpha-treated Sulfite .	40
4.	Mullen Development of Original and Alpha-treated Kraft . .	41
5.	Fold Development of Original and Alpha-treated Sulfite . .	42
6.	Fold Development of Original and Alpha-treated kraft . . .	43
7.	Tear Change with Beating for Sulfite	45
8.	Tear Change with Beating for Kraft	46
9.	Opacity Change with Beating for Sulfite.	48
10.	Opacity Change with Beating for Kraft.	49
11.	Relation of Physical Properties to Alpha-cellulose	51
12.	Hysteresis of Original Sulfite	70
13.	Illustration of a Beaded Fiber	56
14.	Illustration of a Ballooned Fiber.	56
15.	Photomicrograph of Unbeaten Original Sulfite	82
16.	Photomicrograph of Beaten Original Sulfite	83
17.	Photomicrograph of Unbeaten 15 Per Cent NaOH-treated Sulfite.	84
18.	Photomicrograph of Beaten 15 Per Cent NaOH-treated Sulfite	85
19.	Photomicrograph of Beaten Multistage-treated Sulfite . . .	86
20.	Photomicrograph of Unbeaten Rag Stock.	87
21.	Photomicrograph of Beaten Rag Stock.	88
22.	Photomicrograph of Unbeaten 15 Per Cent NaOH-treated Rag Stock.	89
23.	Photomicrograph of Beaten 15 Per Cent NaOH-treated Rag Stock.	90

I

STATEMENT OF PROBLEM

The preparation of wood pulps with a high alpha-cellulose content has been carried out successfully for some time. The patent literature reveals numerous procedures for making such pulps; however, these alpha pulps are characterized particularly by their softness, their permanence, their resistance to hydration, and their absorbency. The fact that these pulps are not easily beaten is a disadvantage. Naturally, the questions arise: (1) Where do the papermaking properties stop as wood pulps are given caustic treatments to make the so-called "alpha pulps", and (2) why do they not possess papermaking properties after a certain point?

In contrast, rag stocks have a much higher alpha cellulose content than ordinary alpha wood pulps; yet these rag stocks possess satisfactory papermaking qualities. Hence, another question arises: What are the differences between rag fibers, which have papermaking qualities, and wood fibers of essentially the same alpha-cellulose content, which do not have these qualities?

This investigation is designed to answer some of the above questions.

II

HISTORICAL SURVEY

A. PULP PURIFICATION

Within recent years, the purified wood pulps high in alpha-cellulose, and therefore called alpha pulps, have advanced from the stage of laboratory curiosities to a position of commercial importance in the paper industry. Schorger (1) aptly described these pulps as being soft, strong, absorbent, and slow hydrating, and Rasch, Shaw, and Bicking (2) have published beating curves for alpha pulps which show these properties.

West (3) has published an Institute of Paper Chemistry bibliography on the preparation and properties of alpha-cellulose which includes seven books, 75 articles, and 146 patents. Jayme (4) also has surveyed the patent literature on this subject.

In general, the methods of purification of wood pulp can be divided into two distinct types. The first consists of treating bleached or partially bleached pulp with hot dilute sodium hydroxide for fairly long periods of time at elevated temperatures (the so-called "hot" process). The second type utilizes concentrated alkaline solutions at moderate temperatures for short periods of time (the "cold" process), and may be used on fully bleached pulps, in which case a mild after-bleach is used. The patent literature contains many references to the use of other materials which may be substituted for the sodium hydroxide, and also to adjuncts to be used with alkali, but these are of more

or less secondary importance.

Jayme (5) has prepared the following table, which gives a comparison of the two treatments:

TABLE I

COMPARISON OF HOT AND COLD ALPHA PROCESSES

	Hot	Cold
Raw material	Partly bleached sulfite	Partly bleached or bleached sulfite or sulfate pulp
Conditions of treatment		
Time, hr.	3-8	1-2
Temp., °C.	82-100	0-20
Pulp consistency, %	9-12	5-10
Concen. NaOH, % by wt.	1/2-1	8-12
NaOH, %, on wt. of pulp	5-8	72-228
Other chemicals present	Reducing, dispersing, buffering, and wetting agents	Wetting and oxidizing agents
Yield, %, from pulp about 87% alpha-cellulose	70-75	85
Alpha-cellulose, %	94	98
Highest alpha-cellulose content obtainable by stressing conditions	96	99
Spent liquor recovery	Not necessary, liquor to waste	Necessary recovery possible by dialysis or burning and causticizing

In this article, Jayme (5) described the preparation of samples by both the hot and the cold process; chemical evaluations,

however, showed that the alpha-cellulose content was insufficient to evaluate alpha pulps. He proposed the use of the swelling behavior and the increase in weight of pulps in 17.5 per cent sodium hydroxide as indications of what he terms the colloid-chemical properties of pulps. He showed that pulps purified to the same alpha-cellulose content by the hot and cold processes differ greatly as regards their two properties; pulps prepared by the hot process swell less and form a denser sheet. Jayme, however, was not concerned with the papermaking qualities of the purified pulps; his main objective was to increase the alpha content and to study the pulps obtained without determining their suitability for any specific use.

The preparation of high alpha wood pulps has also been studied by Rys and Bönisch (6). The effect of the numerous factors in the two processes was very thoroughly investigated, e.g., the time, the alkali concentration, the temperature, etc. The use of other alkalies in place of sodium hydroxide was tried, but none were found to be as good.

Richter (7) has discussed the preparation of alpha pulps from sulfite and sulfate pulps. For acid-cooked pulps, he found that refining by chlorination, hot dilute alkaline digestion, and then an alkaline bleach is very effective. Hot alkaline solvents are not as suitable for alkaline-cooked pulps, probably because the pulps have had no prehydrolysis step due to the alkaline cooking medium, and thus the pentosans are not easily removed by the refining treatment. Richter suggested that the pentosans in sulfite and sulfate pulps are different; in the latter, "alpha" pentosans are present which are not soluble in

dilute alkali. Acid treatment, on the other hand, was said to change the pentosans to the "beta" form, which are soluble in hot dilute alkalies. The probability that this difference in reactivity exists is supported by Klingstedt (5), who reported that even strong sodium hydroxide will not remove pentosans from sulfate pulp. It was noted that concentrated nitric acid effected separation in all cases; however, the character of the pulps from the latter treatment was not given.

To summarize, it may be said that wood pulps are commonly purified by hot dilute or by cold concentrated alkaline treatment. The former is best suited for acid-cooked pulps; with the latter, a preliminary stage involving an acid hydrolysis is required in order to remove the pentosans. ?

B. THE ACTION OF ALKALIES ON CELLULOSE

The whole object of any purification of wood pulp is to remove the materials associated with the cellulose without harming the original condition of the cellulose. Wood consists mainly of cellulose, lignin, hemicelluloses, and resins. Cooking and bleaching are designed to remove the lignin, while the resins and hemicelluloses are normally removed more completely by the alpha treatments mentioned in the foregoing section. It is well known that the resins are saponified in alkaline cooks. Since in the alpha treatments substances more and more intimately associated with the cellulose and more like cellulose chemically are to be removed, some consideration must be given to the effect of these treatments on cellulose itself.

In the hot process, where the concentration of the alkali is

low and the temperature varies from 80° C. to 100° C., the purification reaction must be balanced against the degrading action of the hot alkali in the presence of oxygen. The fact that the cellulose chains can be degraded by this hot caustic treatment is evidenced by the large losses in material occurring in this process, as shown by Jayme (5) and by Rys and Bönisch (6), and also by numerous patents which make use of such materials as sodium carbonate and sodium sulfite to prevent the attack on the cellulose (9). Thus it is seen that the cellulose may be degraded in the hot process but, if the conditions are suitably chosen, this degradation need not be excessive.

In the cold process a different picture presents itself. When the sodium hydroxide is removed by washing, the cellulose is obtained in unchanged form if concentrations of less than about ten per cent by weight are used (10); if stronger concentrations are employed in the treatment, it has been found that, upon removal of the alkali by washing, a changed form of cellulose is obtained, as evidenced by the x-ray diagram (11). This is known as "regenerated cellulose" or "hydrate cellulose." Strictly speaking, the term "regenerated cellulose" should be applied only to cellulose regenerated from solution, which is not the case here; the term "hydrate cellulose" conveys the wrong impression, and therefore in the present work this material will be termed "regenerated cellulose" with the mental reservation that it has not actually been regenerated from a solution.

Chemically, natural and regenerated cellulose are identical, as shown by Miller (12) and by Ost and Westhoff (13). The physical properties are changed, however, principally by the swelling of the

fibers under the influence of alkalies; these changes are indicated by increased hygroscopicity, greater absorption of dyestuffs, and greater reactivity in general (10, 14). The physical changes are also reflected in the x-ray diagrams of the regenerated cellulose, as mentioned briefly above. The lattice appears slightly deformed and widened (15, 16). Such a comparison of the unit cell of the cellulose is given by Marsh and Wood (14); the values for mercerized cotton were taken from data by Andress (11), and those for native cotton from data by Mark (16).

TABLE II

X-RAY DIAGRAMS OF NATIVE AND MERCERIZED COTTON

	Native Cotton	Mercerized Cotton
a	8.35 A°	8.1 A°
b	10.3	10.3
c	7.9	9.1
β	84°	62°

Neale's (17) conception of the action of alkali on cellulose is somewhat as follows: When cellulose takes up water, the hydroxyl groups on the long carbon chains attract water molecules, and, due to the replacing of some secondary cellulose-hydroxyl to cellulose-hydroxyl linkages by water-hydroxyl linkages, the structure expands. In alkaline solutions, especially in concentrated solutions, the cellulose acts as a weak acid, and sodium atoms replace some of the hydroxyl hydrogen atoms formed by the dissociation of the cellulose. The

phenomenon of osmosis takes place, tending to diffuse more water into the structure; the extent of the process depends on the concentration of the alkali. When this sodium hydroxide is washed out, the osmotic pressure falls, and the gel contracts because of its elasticity. This contraction brings secondary hydroxyls again into the sphere of influence of each other, so that more secondary hydroxyl bonds are formed, but not in such great numbers as originally; the orientation of the micelles of the regenerated cellulose is more random than in the original cotton cellulose. If the concentration of alkali is such that mercerization does not take place, the process is merely one of adsorption, and upon washing, the original form of the cellulose is obtained. Morrison, Campbell, and Maass (18) have substantiated Neale's concepts by determining the heats of wetting of cellulose in alkaline solutions.

Thus, in subjecting cellulose to the cold alpha process, the swelling effect must be borne in mind, together with the fact that, when solutions of ten per cent caustic by weight or greater are used, regenerated cellulose will result on washing. D'Ans and Jaeger (19) have shown that this critical caustic concentration is not exact but may vary from nine to twelve per cent caustic depending on the type of cellulosic material in question.

The major constituents which all alpha treatments are designed to remove are the hemicelluloses. This term was coined by Schulze in 1891 (see Dorée (20)) for a group of carbohydrate constituents of the cell membrane which, unlike cellulose, are soluble in dilute alkalies and are readily hydrolyzed to pentoses and hexoses by dilute acids.

In the natural state they are also insoluble in boiling water. Today, the term has taken on a somewhat broader meaning; hemicellulose now includes the noncellulosic carbohydrates, such as pentosans (xylan and araban) and hexosans (mannan, galactan, and possibly glucan), and degraded cellulose, i.e., cellulose of shorter chain length than the alpha-cellulose portion; this degraded cellulose is soluble in strong caustic. In bleached pulp, for instance, the amount of degraded cellulose is usually higher than that of pentosans and hexosans. This has been shown by Heuser (21). It is also well to keep in mind that alpha-cellulose itself is not entirely free of other materials; the pentosans, as mentioned before, are particularly hard to remove. At any rate, hemicelluloses are closely associated with the cellulose and, to remove them, reagents must be used that may affect the cellulose itself. In the hot process, the weak hot sodium hydroxide simply dissolves out the hemicelluloses, leaving the cellulose in an unchanged form. Similarly, in the cold process, the concentrated sodium hydroxide at moderate temperatures dissolves out the hemicelluloses (mainly the degraded cellulosic part), leaving the cellulose in a changed or unchanged form, depending upon the concentration used.

C. FIBER STRUCTURE

Since in this investigation rag stocks as well as wood pulps have been given alpha treatments, the general characteristics of rag fibers and wood fibers should be considered.

A cotton fiber is really a hair which consists of a single long tubular cell with one end attached to the seed (14). It grows

without any attachment to the neighboring fibers. The common impurities encountered are pectic materials, coloring matter, wax, albuminous matter, and inorganic salts. In the cooking of rags with lime, caustic soda, or soda ash, the wax is saponified and is removed together with the pectic materials; bleaching solubilizes the coloring material. All these impurities can be eliminated fairly easily under moderate conditions.

Good reviews of the morphological characteristics of the cotton fiber are given by Denham (22, 23), Bowman (24), and Balls (25). Hall (26) and Clark, Farr, and Pickett (27) have investigated the actual growth of the fiber. They found that for the first thirty days the growth is a matter of increase in length and that the cellulose crystallites laid down during this time show no orientation. Sisson (28) obtained the same results; it will be noted that he also discovered that wax on the fibers may show some orientation under certain conditions. After this first period of ramdom growth, thickening of the walls takes place for the next twenty days, during which the cellulose crystallites are laid down more and more with their long axes in the fiber direction.

Wood fibers, on the other hand, are laid down in trees and are imbedded in lignin. This naturally makes the growth problem more complex; actually, very little is known of the mechanism of growth. Other noncellulosic materials present include, for the most part, inorganic salts, resins, and hemicelluloses. In wood, the type of fiber depends largely upon the season during which it is formed. Those grown in the spring have thin walls and large lumen, as compared

with the thick-walled summer fibers. The wood may be cooked in an alkaline or an acid medium to remove the lignin. In an alkaline cook a pulp is obtained with more ash, more lignin, less resin, and with a lower yield than that obtained in an acid cook. Bleaching procedures are used to remove residual lignin.

Mahood and Cable (29) have compared highly purified wood pulp and rag stocks as regard their chemical properties. They showed that rag stocks have less hemicelluloses and pentosans. Lewis (30) also showed the same differences in the chemical properties of rag stocks and alpha wood pulps.

Once the rag stock or wood pulp is obtained, neglecting the difference in impurities, the gross structure of the two types of fibers is quite similar. Nägeli (31) in 1858 proposed the micelle theory for starch and cellulose. Ambronn (32) stated that double refraction of the fibers was due in part to minute rodlike particles or crystals which lie parallel to each other. Recent views on fiber structure have been given by Ludtke (33) and Ritter (34). They consider the fibers to be composed of a central lumen, with fibrils forming the secondary walls. Ludtke believes that there are transverse elements in the fibers, but Ritter does not. The fibrils are arranged in concentric layers. On the outside layer of the fibers, the fibrils are arranged almost at right angles to the fiber axis for wood fibers and at an angle of about forty-five degrees for rag fibers. Nearer the lumen, the fibrils become arranged more parallel to the fiber axis. Balls (35) has published data which show that there may be twenty to twenty-five of these concentric layers in rag fibers. Farr and Eckerson (36) have

claimed that the action of pectic solvents, the absence of double refraction, and the staining reaction with Ruthenium Red indicate the presence of a pectic substance which cements small discrete bundles of cellulose crystallites together. In a later article, Farr (37) further claimed evidence to show the presence of this cementing substance. Anderson and Kerr (38) disagreed with Mrs. Farr's work and gave evidence to show that the cellulose is present as very thin threads. Growing cotton under constant light and temperature conditions gave a fiber with no growth rings, and they therefore concluded that there are no sheaths between the concentric layers, but that growth rings simply represent dense and less dense areas of cellulose. Thus, they accept the micelle theory. Be this as it may, it is seen that, in a gross sense, purified wood and rag fibers are quite similar morphologically. It is true that submicroscopic differences are readily discernible, but these are of less direct importance to the problem at hand.

In the matter of size, wood fibers and rag fibers differ markedly. According to Ritter (34), both are about 0.03 mm. in diameter, but rag fibers average 35 mm. in length versus a length of about three mm. for softwood fibers. Thus, rag fibers have a length to width ratio of 1200, as compared with 100 for wood fibers.

D. BEATING

From the papermaking viewpoint, any property of pulp is interesting, but in the final analysis its most important characteristic is the one which determines the kind of sheet which can be made from it and the properties of this sheet. The papermaking qualities of a pulp are evaluated by beating. The mechanism of beating is still

little understood; however, according to Campbell (39), any beating theory must account for seven noticeable changes in the pulp. They are:

1. Increased fibrillation
2. Slimy or greasy feel
3. Increased shrinkage on drying with production of a dense paper
4. Low freeness and reluctance to part with water
5. Increased tensile and bursting strength of paper with a low tear
6. Increased transparency
7. Increased degree of color with dyes

The first ideas of what happened during beating were interpreted in a chemical sense. Minor (40) was one of the adherents of this chemical theory of beating. She presented evidence which indicated that, because of the increase in copper number on beating, because of the fact that the highly beaten stock holds more water in the paper form than the free stock does, because of the high shrinkage of beaten stocks on drying, and because of a slight lowering in viscosity, a chemical compound was formed. All these results, however, have not been substantiated by other investigators. Schwalbe and Becker (41) had previously found beaten pulp to be more hygroscopic than unbeaten pulp, though their method was rather crude.

The chemical theory was discredited by the work of Strachan (42), who found that there can be no hydration in the chemical sense, since the curve of the vapor pressure of beaten pulp plotted against

the water content was continuous. Furthermore, there was no difference in the end product, dry cellulose. Strachan believed that the main difference between beaten and unbeaten pulp is in the water which the cellulose has imbibed during swelling, and that the mechanical action of beating increases the surface area exposed, thereby increasing the rate of imbibition. This is a purely physical view. In a later paper, Strachan (43) argued that the strength increase is due mainly to increased fibrillation and resulting fiber entanglement. Data were presented to show that on beating there is no increase in the total surface of the pulp. Clark (44) showed that boiling water will destroy hydration but does not seriously affect the strength of the pulp. Thus, perhaps water of imbibition and flexibility are not as important as is often thought. Bell (45) attempted to break down the various actions of beating and to explain their effect. According to his conception, the separation of fibers will give orientation, uniformity, and strength; the cutting and fibrillation will delay drainage, aid felting, lower porosity, and increase strength; while the colloidal surface film formed will promote cohesion and strength, give lower porosity and undesirable shrinkage. Edge (46), however, fibrillated fibers in toluene and, as the sheets had no strength, he concluded that it is not fibrillation which gives strength on beating. Porvik (47) used alcohol and reached the same conclusion. Bailey (48), using purely microscopical methods, found that long beating produced "cylindricoids," finer fragments, and a clear gel--all cellulosic in nature. Thus, fibrillation seems to be a minor factor in strength, and the formation of a gel has been shown.

Other authors have offered various explanations of the

mechanism of ~~bleaching~~. Campbell (39) cited unpublished work by Pidgeon, who, with the use of refined procedures, showed that beating did not make pulp more hygroscopic. Seborg and Stamm (49) found the equilibrium moisture content of beaten and unbeaten pulp to be the same at various humidities, and also found the contained water the same, as shown by electrical conductivity data. Apparently, then, the degree of hydration, or the total surface, is not changed appreciably, and some other explanation must be attempted. Campbell believed that in water all cellulose surfaces are in a hydrated or wetted condition and that beating simply bruises fibers so that more internal surfaces are exposed; thus, the fiber-to-fiber bonds are increased on drying.

Curran, Simmonds, and Chang (50) found no effect on chemical properties after beating sulfite and sulfate pulps except an increase in rate of hydrolysis due to increased subdivision. Kress and Bialkowsky (51) confirmed the observations that there are no chemical changes except a slight drop in cuprammonium viscosity. They found that beating in liquids which do not wet the pulp simply cuts the fibers without developing fibrillae. The freeness was about the same in spite of the differences in fineness. Beating in ethylene glycol and formamide, which wet cellulose, gave results much as in water. Highly beaten pulp, air dried to a horny mass, recovered its original condition after soaking several days, though sheets made from it were not quite as strong as from the original pulp. They concluded that swelling makes the fibers ductile and plastic so that mechanical action bruises and fibrillates, and that the action is not all cutting. Campbell (39) has calculated the effects of surface tension and

believes this may be a large factor in forming sheets. Doughty (52) showed that subjecting unbeaten pulps to high pressure, so that the sheet density was reduced to that produced by beating, gave the Mullen development and tear decrease just as in beating. Thus, reduction of fiber length is not necessary for strength development for wood pulps.

The actions causing the various changes on beating are summarized by Campbell (39) as follows:

1. Fibrillation--mechanical effect, but the fiber must be swollen
2. Greasy feel--simple subdivision
3. Low freeness--fibrillation and cutting makes lower effective pore diameter
4. Shrinkage--surface tension effects
5. Increased strength--increased density, meaning more fiber-to-fiber contacts
6. Increased transparency--increased density meaning more fiber-to-fiber contacts

The causes of the effects of beating are far from a closed book. The above list contains some of the more recent explanations. Until more work has been done, no definite conclusions may be drawn, but pulps will still be evaluated by beating procedures.

E. SORPTION OF WATER VAPOR

Two of the very important characteristics which cellulose possesses are the sorption of water vapor and the swelling of the fibers in suitable liquids. Both of these are properties possessed,

in general, by gels; therefore cellulose acts like a gel. Hence, this might be a good method of distinguishing between colloidal systems of two pulps. In other words, what effect do alpha treatments have on the colloidal or gel structure of cellulose?

Weidner (53) has published a very thorough bibliography on sorption effects in general. Literature is cited to show that many and varied kinds of cellulosic materials have been investigated; that the presence of air has little effect on hysteresis in water vapor sorption; and that beating increases the moisture content slightly. Literature also shows that there is an irreversible loss in hygroscopicity of cellulosic materials during the primary desorption.

Of more importance to this work is the effect of purification of cellulose on the water vapor sorption and the characteristics of regenerated cellulose. Fay (54) reported in 1926 that bleached pulp sorbed less water than unbleached. This conclusion was also reached by Urquhart, Bostock, and Eckensall (55). Seborg, Simmonds, and Baird (56) found that bleaching silver fir sulfite pulp lowered the hygroscopicity as much as 13.4 per cent throughout a relative humidity range of 93 per cent. Weidner (53) also found that bleaching reduces hygroscopicity, but only to about the same amount as beating. At any rate, purification of pulp or rag stock by bleaching decreases the hygroscopicity.

There is apparently no data in the literature on the sorption of water vapor by alpha wood pulps.

Mercerized cotton cellulose has received considerable attention.

Urquhart, Bostock, and Eckersall (55) found that mercerized cotton has a very great sorptive capacity and that this is continually reduced as the material is desorbed for the first time. Urquhart and Williams (57) also found that mercerized cotton has greatly increased hygroscopicity, and their findings have been substantiated by a large number of other investigators. Urquhart and Williams further found that the ratio of the adsorption of the treated to untreated cellulose was constant over the whole humidity range and designated this as "the mercerization ratio." This ratio varied with the conditions of the caustic treatment and was similar to the effect on the length and degree of swelling of the cotton. Balls (25) gave curves of the percentage water-percentage humidity relation and showed that mercerized cotton not only adsorbs more water but has a wider hysteresis loop; however, he also mentioned that this water must be held in a different manner than that in natural cellulose for, although the mercerized cellulose is wetter at any given humidity, this mercerized material is a poorer conductor of electricity.

Thus, cellulose exhibits a hysteresis effect when sorbing water vapor. Purification by bleaching lowers the hygroscopicity, but mercerization treatments increase this hygroscopicity; the water, however, seems to be held in a different manner.

F. OPTICAL PROPERTIES

Since beating results in increased transparency of sheets, an investigation of the general optical concepts of sheets might prove to be of interest.

When light is incident on paper or on any other opaque material, part of it is transmitted, part is reflected or scattered, and the remainder is absorbed. Three separate equations have been independently derived relating the diffuse reflectance of homogeneous materials in terms of fundamental constants of the material; these are the equations of Ryde (58), Guerevic (59), and Kubelka and Munk (60). The latter is more obviously related to physical phenomena. The equation is:

$$k/S = (1 - R_\infty)^2/2R_\infty$$

where

k is the absorption coefficient of the material,

S is the scattering coefficient of the material, and

R_∞ is the reflectance of an opaque pad.

The application of this equation to paper surfaces has been shown by Steele (61) and Judd (62). Graphs were made which permit the calculation of R_∞ from R_0, the reflectance of a single sheet backed by black, and $R_{.98}$, the reflectance of a single sheet backed by magnesium oxide. Likewise, the scattering coefficient for a thickness x, i.e., Sx, can be obtained from R_0 and $R_{.98}$, or the opacity can be computed.

The opacity or contrast ratio of a paper is defined as the ratio of its reflectance over a black background to its reflectance over a white one. If the white is magnesium carbonate, the contrast ratio is $C_{.98}$, because magnesium carbonate has a reflectance of 0.98. The reflectance of the black is assumed to be zero. In the case of TAPPI opacity, the white has a reflectance of 0.89, and the designation is $C_{.89}$. Foote (63) has listed the factors governing the opacity of a sheet as: (1) the reflection from the initial surface; (2) reflection

at each cellulose-air interface within the sheet; (3) absorption of light by the fibers, and (4) multiple reflection and refraction within the sheet.

Lewis (64) believed that transparency is merely obtaining the right sheet structure by eliminating fiber-air interfaces. Wicker (65) agreed with this idea and derived equations to show that air-cellulose interfaces have a much larger effect in interfering with the passage of light rays than cellulose-cellulose interfaces. He listed as transparency factors: (1) mechanical structure of the sheet; (2) surface smoothness; (3) foreign materials; and (4) optical contact of the fibers in the sheet.

Thus, some of the factors in the increased transparency and decreased opacity observed on beating have been recorded in the literature, and an equation relating the diffuse reflectance with fundamental constants has been developed.

III

MATERIALS AND METHODS

A. PULPS USED

The three stocks selected for this investigation included a bleached Mitscherlich sulfite (chosen for its easy beating characteristic), a bleached kraft, and a high grade bleached rag stock prepared from No. 1 white shirt clippings.

These stocks were received in the wet condition, containing about 75 per cent water, and were used without further drying. Each of the original materials was given a washing procedure as follows: The pulps were broken up in the water at 3 per cent consistency with a Lightnin' mixer, were washed with hot water for 5 minutes and then with cold water for 3 minutes. After washing, the material was pressed to about 25 per cent dryness, broken up by hand, and stored in an air-tight container. Samples were withdrawn from this supply as needed.

B. PREPARATION OF SAMPLES

1. The Hot Process

Hot treatments were given the sulfite pulp as follows: The equivalent of 3 pounds of oven-dry stock was diluted in a 22-liter flask with enough sodium hydroxide of the desired concentration to give 3.9 per cent consistency. Three different concentrations of alkali were used, namely, 1/2, 1, and 2 per cent sodium hydro

solution by weight. Two per cent sodium sulfite on the weight of the pulp was added to reduce oxidation. The mixture was stirred in a flask with a stainless steel mixer. The temperature was raised to 93° C. as rapidly as possible in a water bath heated by a gas flame. This temperature was maintained for 3 hours.

After the treatment the pulps were drained, washed with hot water for 15 minutes or until the wash water was neutral to litmus. Then the washed pulp at 4 per cent consistency was stirred with 1 per cent acetic acid by weight for 5 minutes to remove the last traces of alkali. After this period the pulp was again washed with hot water for 5 minutes, pressed to about 25 per cent dryness, and broken up by hand.

A second batch was then made as described above. In all, this furnished the equivalent of 6 pounds of oven-dry stock treated at each concentration of alkali.

The rag stock could not be circulated in the standard equipment because of its stringy nature. In an attempt to reduce the strings, several beater runs were made at low consistencies to determine whether the stock could be shortened without hydration, but this operation proved unsuccessful. Some of the stock was then shredded in a 7-1/2 h.p. Williams disintegrator, but this attempt, too, was unsuccessful; although the stock could be shortened somewhat, the long strings clogged the machine. The third alternative of cutting the stock by hand was too laborious to consider.

In the end, the rags were cooked in a stainless steel digester equipped with a circulating system. At the end of the treatment, the

stock was removed from the digester by hand. Apart from this, the conditions of the hot treatment and washing of the rag stocks were exactly the same as those for the sulfite pulps.

It might be mentioned that the kraft pulp was not given a series of hot treatments because, as indicated in the Historical Survey, alkaline-cooked wood pulps have been shown to resist purification by hot dilute alkaline treatments.

2. The Cold Alpha Process

For the cold process, the equivalent of 6 pounds of oven-dry stock was treated for 1 hour with 5, 10, and 15 per cent sodium hydroxide solutions by weight, respectively, at 3.6 per cent consistency and at 20° C. Stirring was occasional. After the treatment, the washing was the same as that explained above for the hot process, except that the stocks from the treatments with 15 per cent sodium hydroxide were given 2 acetic acid washes.

Cold alkaline treatments were given to rag and kraft with 5 and 10 per cent sodium hydroxide, and to rag, kraft, and sulfite with 15 per cent sodium hydroxide.

C. CHEMICAL EVALUATION OF THE PREPARED SAMPLES

The yield was obtained on all the treatments simply by determining the gross weight before and after treatment and correcting for the moisture contents of the samples.

For chemical testing, the pulps were not air-dried, but water was removed from the samples which had been prepared for analysis

by treating them successively with 95 per cent ethyl alcohol, absolute alcohol, and absolute ether. The samples were spread out to allow the ether to volatilize and were then shredded in a Gösta-Hall disintegrator and stored in Mason jars.

The following tests were determined on duplicate samples of all the pulps:

Alpha-cellulose	Institute Method 421
Cuprammonium viscosity	420
Copper number	609
Pentosans	424
One per cent sodium hydroxide solubility	450

D. BEATING CHARACTERISTICS OF THE WOOD PULPS

The entire members of the series were beaten in a calibrated 1-1/2-pound Valley laboratory beater. They were then evaluated according to the following methods:

Basis weight	Institute Method 504
Caliper	508
Mullen	510
Fold	513
Tear	512
Opacity	518

From these tests and the Schopper-Riegler freeness data, beater curves were drawn and the properties of all pulps were evaluated by interpolation at 500 cc. freeness.

E. BEATING CHARACTERISTICS OF THE RAG STOCKS

Unfortunately, the 1-1/2-pound Valley laboratory beater is not sturdy enough for evaluating rag stocks.

A 5-pound Valley beater with movable bedplate was tried and found, after some study, to give satisfactory results. At first, the consistency was varied to determine the optimum value. Then the weight on the bedplate arm was changed so as to find the condition which produced the best beaten rag stock. Experiments indicated that 19.5 pounds on the bedplate arm and a consistency of 2 per cent would give beaten handsheets with strength values comparing fairly well with those obtained commercially. These conditions were employed in the rag stock beater tests. Only two pounds of stock were available for the beater run; it was observed that if more than 2 or 3 sets of handsheets were made, the stock reached such a low level that circulation stopped. The procedure used, therefore, was to determine the Schopper-Riegler freeness at regular intervals and make only two sets of sheets, somewhere between 500 cc. and 300 cc. freeness.

The sheets were made and tested as described in the previous section, with the exception that the stocks were evaluated at 350 cc. freeness.

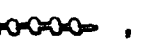
F. SWELLING CHARACTERISTICS OF THE SAMPLES

1. Cuprammonium Swelling

It has been suggested that the manner in which fibers swell in cuprammonium hydroxide solution is a good indication of their amount

of cooking, their ease of acetylation, and, in short, the past history of the fiber. The swelling of these treated stocks in cuprammonium hydroxide was therefore investigated.

Slides were made of the different samples as follows: Two small strips of thin paper were placed along the edges of a microscope slide, and the fiber suspension was placed on the slide. After the fibers were straightened somewhat by means of two dissecting needles, a cover glass was fastened at the sides by two small strips of adhesive tape. The thin paper strips, acting as wedges, were just thick enough to permit the passage of the swelling liquid between the slide and the cover glass, but at the same time the fibers were kept from floating along in the liquid.

Standard cuprammonium solution for viscosity determinations (200 grams per liter of ammonia and 15 grams per liter of copper) was diluted to make solutions of from 10 to 60 per cent normal strength. These were kept in ice water. First, 10 per cent solution was drawn into the slide by placing a drop of this solution on one edge of the cover glass and drawing it in by applying a blotter to the other side. A typical field had previously been selected and was in focus under 250 magnification. When no more action was noted, the field was viewed, and the approximate percentages of swollen and unswollen and ballooned and beaded fibers were noted. Beading is indicated by the following structure,  , and ballooning, ; see Figures 13 and 14. Following the initial swelling, a 15 per cent solution was added, and the process repeated. This was followed by a 20 per cent solution and by stepwise increase in cuprammonium

concentration until practically all the fibers had dissolved. About 40 fibers were viewed.

2. Swelling in 17.5 Per Cent Sodium Hydroxide

Jayme (5) has suggested that the linear extension and weight increase of pulp pads in 17.5 per cent sodium hydroxide give a good characterization of the pulps; hence, a method was developed which was patterned after that of the Faserstoff-Analysenkommission des Vereins der Zellstoff- und Papier-Chemiker und -Ingenieure (66).

Heavy sheets (176 lb.--25x40-500) of the unbeaten pulps were made on the Noble and Wood sheet machine. These were pressed between felts at 150 pounds per square inch for 5 minutes and air-dried for 16 hours on the forming wires to prevent shrinkage and cockling. From these air-dry sheets, discs 3.2 cm. in diameter were stamped out and holes 0.78 cm. in diameter were punched through the center of the discs by means of a paper punch. Thirty of these discs were centered on a piece of glass tubing with a No. 10 rubber stopper on the bottom. This was first tared and weighed, and then 700 grams of weights were placed on the discs, and the height in millimeters before swelling was measured. Three hundred cc. of 17.5 per cent sodium hydroxide at exactly 20° C. were added after the weight had been removed. The discs were allowed to swell 15 minutes, the weight was again added, and 5 minutes after the addition of the weight the swollen height was again measured. The discs were removed from the liquor and allowed to drain under the force of the weight for 5 minutes, after which time the excess liquor was removed by means of a paper towel, and the discs were

weighed. From these data, the percentage of weight increase, the percentage of height increase, and the swelling volume were calculated.

G. DETERMINATION OF FACTORS CAUSING INCREASED OPACITY OF PULPS

One of the results of this investigation must be anticipated at this point. It was found that in certain pulps the opacity increased with beating. This change was of a magnitude which showed that it was actually a real phenomenon.

To obtain optical data on this opacity increase, the Kubelka and Munk equation (page 19) was used. The reflectances, R_0 and $R_{.98}$, were obtained with the General Electric recording spectrophotometer, and from these two values R_∞ and "Sx", the scattering coefficient for a thickness x, were evaluated by use of suitable charts prepared by Steele (61). Thus, the absorption and scattering coefficients, k and S, were determined.

H. EQUILIBRIUM MOISTURE OF SHEETS

British sheets weighing about 4 grams were made of all the pulps, air-dried in the usual manner, and seasoned at 65 per cent relative humidity and 70° F. for 48 hours or more. The sheets were then placed in weighing bottles, and the moisture content was determined.

I. EFFECT OF RELATIVE HUMIDITY ON FIBER WIDTH

The apparatus used was that employed by Weidner (53). Relative humidities of 58 and 95 per cent were obtained by bubbling air

through saturated salt solutions (manganous chloride and di-sodium phosphate, respectively) at exactly 25° C. Zero per cent relative humidity was obtained by passing air through a drying series consisting of calcium chloride, concentrated sulfuric acid, and phosphorous pentoxide suspended on cotton.

The air of predetermined humidity was passed through the special cell designed by Weidner (53) which accommodates a slide on which the fibers in question are placed. The changes in width of these fibers with relative humidity change was determined by actually measuring the fiber width changes by the use of a Filar micrometer and 250 magnification.

Slides of the water suspensions of the pulps were made so that about 40 fibers were taken and arranged by the use of 2 dissecting needles. The slide was then placed in the cell, and air of 95 per cent relative humidity was introduced. The excess water soon evaporated. A drawing was made noting the location of each fiber to be measured as indicated by the reading on the mechanical stage used, and as indicated by easily recognizable spots on the fibers, e.g., where one fiber crossed another, where a fibril was located, where large bordered pits were noticeable, etc. Thus the same spot on the fiber was always measured.

After three hours at 95 per cent relative humidity, the diameters of the fibers were measured. Then air of 58 per cent relative humidity was passed through the cell for at least 20 minutes to allow for equilibrium, and the widths were again measured. In a like

manner the widths at zero per cent humidity, 58 per cent, and 95 per cent relative humidity, and a second complete cycle were determined. That the time allowed for the system to come to equilibrium is sufficient is shown by the fact that no change in fiber dimensions could be detected after 5 minutes had elapsed at the humidities studied.

It will be noted also that only 40 fibers of about the same size were measured. Weidner (53) found that 200 fibers of all sizes had to be measured to reduce the probable error to about 3 per cent; but in his original work, he arranged the fibers according to size and found that fibers of different widths but similar lengths changed by about the same percentage. Thus, in this case, measuring 40 fibers of nearly the same size resulted in a probable error of less than one per cent, and yet the data obtained were indicative of the action of fibers of all sizes.

Only the pulps which should show noticeable differences were measured. These were:

1. Original sulfite, rag, and kraft
2. Hot 2 per cent alkali-treated sulfite and rag
3. Cold 15 per cent alkali-treated sulfite, rag, and kraft

J. CAPILLARY RISE IN SHEETS

F. A. Simmonds (67) has found that when strips of unsized paper are immersed in water, there is a straight line relation between the log time and the log height of capillary rise of the water in accordance with theory (68). Lucas (68) has derived the fundamental equations which permit the effective capillary diameter of any capillary

structure to be calculated from the rate of the height of rise of liquids in the material in question. By integrating Poiseulli's law and substituting the force due to the surface tension rise in capillaries, the following equation was derived:

$$h^2 = (Srt)/2v,$$

where

h is the height rise,

S is the surface tension,

r is the effective capillary radius,

t is the time, and

v is the viscosity of the liquid.

This equation has been shown to be experimentally correct if used for heights of rise much less than the equilibrium height (so that the driving force is essentially constant)and if the capillary structure is fine and the liquid wets the capillary walls completely. Expressed more simply, the equation is

$$h^2 = kt,$$

where

k is a constant.

If this equation is applied to the data concerning rate of rise of a liquid in a strip of paper, the constant k can be evaluated. Since

$$k = (Sr)/(2v),$$

the effective capillary diameter, D, is

$$D = (2kv)/S.$$

In this manner the effective capillary diameters of the sheets in question were evaluated.

The equivalent of 20 grams of oven-dry pulp was disintegrated in 2 liters of water in the British disintegrator for 3000 revolutions. Then, 50-pound sheets (25x40-500) were made, pressed at 75 pounds per square inch for 5 minutes, air-dried, and seasoned at least 6 hours before testing.

The apparatus used was simple; nevertheless, results have shown that the method is internally consistent. Strips of the sheets, 13.2 cm. in length and 15 mm. in width, were immersed exactly 10 mm. into a pan of water, a stop watch was started at the same time, and the height of rise was taken at intervals of 10 minutes. Simple paper clamps served to hold the paper vertically in the water. The entire procedure was carried out at 70° F. and 65 per cent humidity. The interface of the water rising in the strip could best be observed by placing an ordinary desk lamp behind the apparatus; in the transmitted light, the boundary showed up very clearly.

IV

RESULTS AND DISCUSSION OF RESULTS

A. YIELD AND CHEMICAL CONSTANTS OF THE PREPARED PULPS

The yield data and chemical constants of the pulps prepared are given in Table III.

The yields for the hot process are lower than those for the cold process. This is due to the fact that in the hot treatment, besides purification, more degradation takes place than with the cold treatment. The relative rate of purification and degradation depends upon the concentration of the alkali, the temperature, the resistivity of the pulp, the absence or presence of oxygen, and numerous other factors, all of which contribute to lower yields for the hot process.

The alpha-cellulose content of the rag stock is not raised very greatly by either the hot or the cold treatment. Presumably, this is a material that is so pure that these methods are not active enough, or else the nature of the impurities are such that they are not rendered soluble by concentrated or dilute alkaline treatments.

In the hot process the viscosity values showed a slight increase for the sulfite pulp until 2 per cent sodium hydroxide was used, and then the viscosity dropped. Thus, from the standpoint of viscosity, at 2 per cent sodium hydroxide concentration the degradation action was faster than the purification. There are at least two factors which may influence the viscosity: (1) the removal of soluble materials, such as hemicelluloses, which should increase the viscosity

TABLE III

CHEMICAL ANALYSES OF PREPARED PULPS

Sulfite (Mitscherlich)

Treatment and % NaOH	Yield %	Alpha Cellulose	Viscosity cp.	Copper Number	Pentosans %	1% NaOH Solubility
Original	100	80.88	26.10	3.57	6.18	13.29
Hot 1/2	88.4	85.21	29.99	1.25	5.76	5.75
Hot 1	85.5	86.5	28.07	0.88	5.75	4.14
Hot 2	83.5	88.05	26.26	1.01	5.82	2.66
Cold 15	84.7	95.17	28.56	0.96	1.83	3.92

Rag Stock

Original	100	96.00	234	0.210	0.93	2.11
Hot 1/2	96.6	96.32	198	0.072	0.76	1.74
Hot 1	94.0	96.83	165	0.067	1.01	1.69
Hot 2	92.0	96.37	104	0.117	0.89	1.99
Original	100	96.00	234	0.210	0.93	2.11
Cold 5	98.0	96.23	131	0.204	0.58	2.14
Cold 10	97.0	96.47	117	0.710	0.44	2.05
Cold 15	96.2	97.32	228	0.045	0.69	2.23

Bleached Kraft

Original	100	81.36	14.15	1.11	9.47	7.86
Cold 5	95.6	86.37	13.11	0.88	5.79	5.57
Cold 10	90.2	91.76	13.81	0.55	2.57	4.23
Cold 15	88.0	93.25	13.22	0.51	2.46	4.60

values, and (2) oxidation, which should lower it. In addition, particularly in the case of the hot process, the cellulose itself may be attacked somewhat and the viscosity lowered. In the case of the rag stock, even the 1/2 per cent alkali treatment lowered viscosity. This may have been caused by the fact that there are so few impurities to react with the sodium hydroxide that the full power of the action was felt by the cellulose; in other words, the cellulose is not protected by the presence of other materials having a greater tendency to react with the alkali. The evaluation of viscosity data, however, is very complicated, and definite conclusions could be drawn only if both the purification and the degradation were investigated separately.

The copper number data show practically the same results as the viscosity data.

The data as a whole show that the hot process does not remove pentosans very effectively, and yet other constituents are removed from the sulfite as shown by the decrease in the 1 per cent sodium hydroxide solubility tests. The yield of pulp is also lower with the hot alkaline treatment than with the cold.

B. BEATING CHARACTERISTICS OF THE WOOD PULPS

The data for the beating characteristics of the various wood pulps are given in Tables IV and V and shown graphically in Figures 1-10.

The rate of freeness drop is shown in Figures 1 and 2. The data for the sulfite pulp (Figure 1), demonstrate that the hot process did not lower the rate of freeness drop very greatly; however, the

TABLE IV

BEATING CHARACTERISTICS FOR SULFITE

Original Sulfite

Time min.	Freeness cc.	Basis Weight 25x40-500	Caliper mils	Apparent Density	Mullen pts./#	Tear Factor	Opacity	M.I.T. Fold
0	860	48.4	3.5	13.8	50	1.52	66.8	36
20	625	48.0	2.9	16.5	100	0.73	53.1	915
40	275	46.8	2.5	18.7	88	0.58	44.6	2221
			Hot 1/2% NaOH Treated Sulfite					
0	865	49.0	4.5	10.9	14	1.83	77.2	3
20	710	47.0	4.0	11.7	83	1.00	69.4	315
40	445	46.7	2.8	16.7	84	0.75	69.4	438
60	250	47.0	2.6	18.1	89	0.61	59.0	1643
80	175	45.8	2.5	18.3	76	0.52	52.1	1637
			Hot 1% NaOH Treated Sulfite					
0	860	48.6	4.5	10.8	14	1.84	79.0	3
20	725	47.1	3.1	15.2	79	1.02	71.8	204
40	455	46.8	2.9	16.1	75	0.85	71.8	388
60	305	47.4	2.8	16.9	78	0.72	63.4	749
80	200	46.7	2.5	18.6	75	0.60	60.5	716
			Hot 2% NaOH Treated Sulfite					
0	860	49.2	4.3	11.4	12	1.56	79.0	0
20	700	47.0	3.1	15.2	66	1.02	73.8	74
40	470	48.0	2.9	16.5	77	0.80	71.3	258
60	330	48.0	2.8	17.1	71	0.73	66.1	336
80	220	48.4	2.8	17.3	72	0.65	57.8	373
			Cold 15% NaOH Treated Sulfite					
0	860	46.8	5.8	8.1	13	0.41	68.0	0
20	855	46.2	5.0	9.2	13	1.11	72.9	0
40	850	45.8	4.5	10.2	15	1.11	73.2	2
60	845	45.8	4.2	10.9	17	1.11	74.3	2
80	780	46.0	4.1	11.2	20	0.89	76.1	2
100	750	46.6	4.1	11.4	19	0.90	77.6	3
120	665	44.1	3.8	11.6	23	0.80	81.7	2
140	600	45.2	3.7	12.2	22	0.71	83.4	2
160	530	45.2	3.5	12.9	22	0.60	83.4	2
180	500	44.4	3.4	13.1	23	0.54	87.0	2
200	460	44.1	3.2	13.8	20	0.46	89.6	2
220	400	45.5	3.2	14.2	18	0.39	89.0	3

TABLE V

BEATING CHARACTERISTICS OF KRAFT

Original Kraft

Time min.	Freeness cc.	Basis Weight 25x40-500	Caliper mils	Apparent Density	Mullen pts./#	Tear Factor	Opacity	M.I.T. Fold
0	845	47.4	4.0	11.8	44	2.02	75.7	31
20	790	45.8	3.2	14.3	96	0.94	69.1	599
40	585	46.4	3.0	15.5	101	0.83	66.5	847
60	380	45.8	2.9	15.8	103	0.77	60.0	1059
80	230	46.3	2.8	16.5	93	0.66	56.2	996
			Cold 5% NaOH Treated Kraft					
0	840	47.0	4.3	10.9	28	2.10	79.0	11
20	795	46.3	3.5	13.2	76	1.11	71.2	148
40	625	46.2	3.1	14.9	89	0.93	69.8	357
60	430	46.5	3.0	15.5	84	0.81	68.4	412
80	295	47.4	3.0	15.8	89	0.77	65.0	472
100	210	47.4	3.0	15.8	89	0.73	60.4	828
			Cold 10% NaOH Treated Kraft					
0	855	48.4	5.5	8.8	12	1.26	77.7	0
20	855	48.3	4.5	10.7	31	1.95	74.4	18
40	805	47.6	4.0	11.9	44	1.38	75.0	27
60	695	47.6	3.8	12.5	48	1.18	76.4	32
80	550	46.5	3.5	13.3	45	0.99	79.3	21
100	440	46.6	3.2	14.6	47	0.90	81.5	31
120	350	47.4	3.1	15.3	49	0.79	79.5	44
140	255	47.4	3.0	15.8	46	0.73	80.0	48
			Cold 15% NaOH Treated Kraft					
0	850	49.8	7.0	7.1	12	0.63	70.6	0
20	850	49.4	5.5	9.0	12	1.39	71.2	0
40	850	49.0	4.8	10.2	22	1.47	72.2	3
60	795	48.6	4.2	11.6	25	1.28	74.8	4
80	680	48.4	4.1	11.8	25	0.87	76.6	5
100	545	48.5	4.0	12.1	27	0.74	80.7	6
120	445	48.3	3.7	13.0	29	0.67	85.4	7
140	345	49.4	3.5	14.1	28	0.60	84.5	7

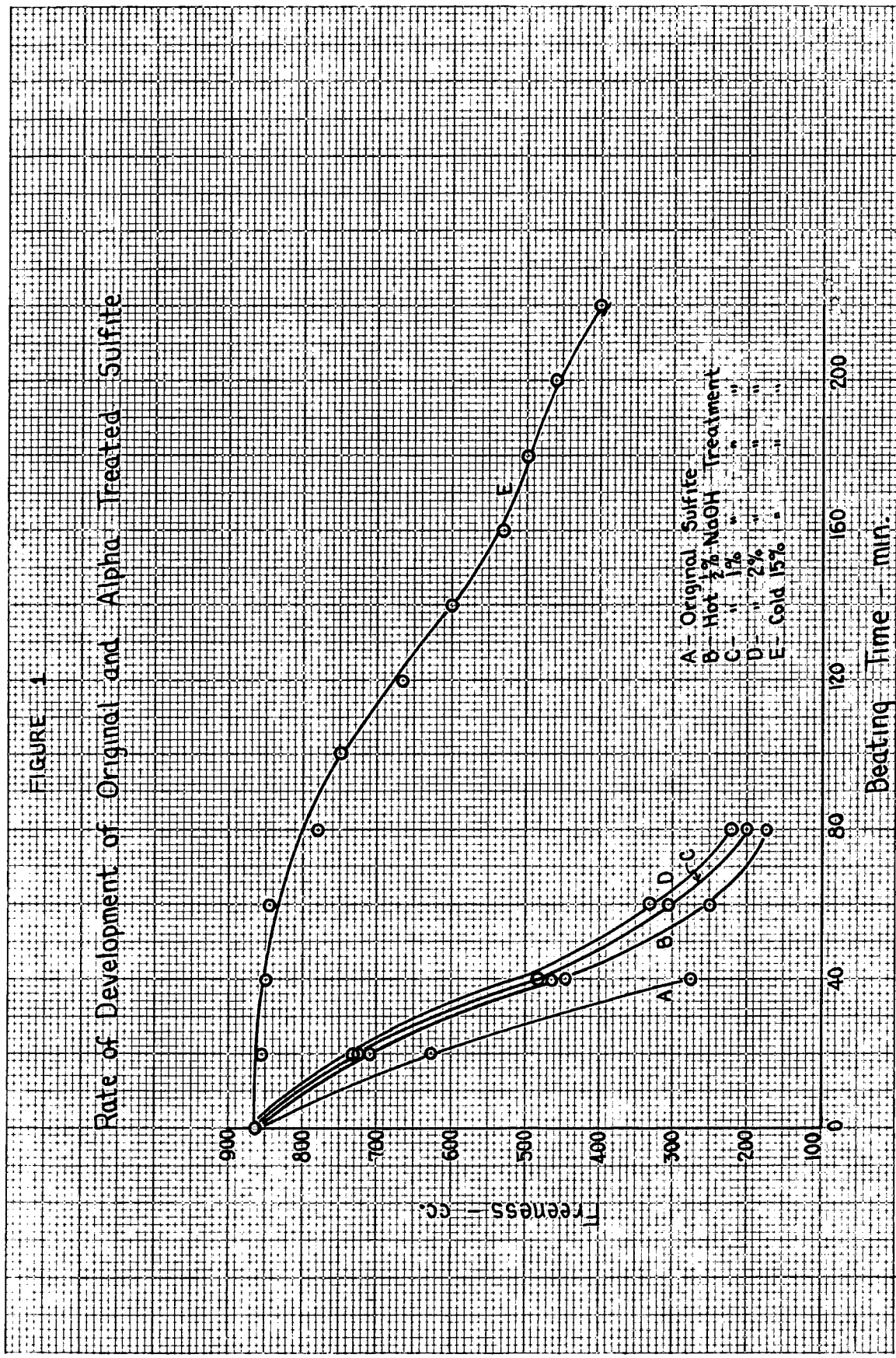


FIGURE 1
Rate of Development of Original and Alpha Treated Sulfite
Freeness — cc.
900
800
700
600
500
400
300
200
100
0
40
80
120
160
200
Beating Time — min.
A
B
C
D
E
A— Original Sulfite
B— Hot 1% NaOH Treatment
C— " 1% " " "
D— " 2% " " "
E— Cold 15% " " "

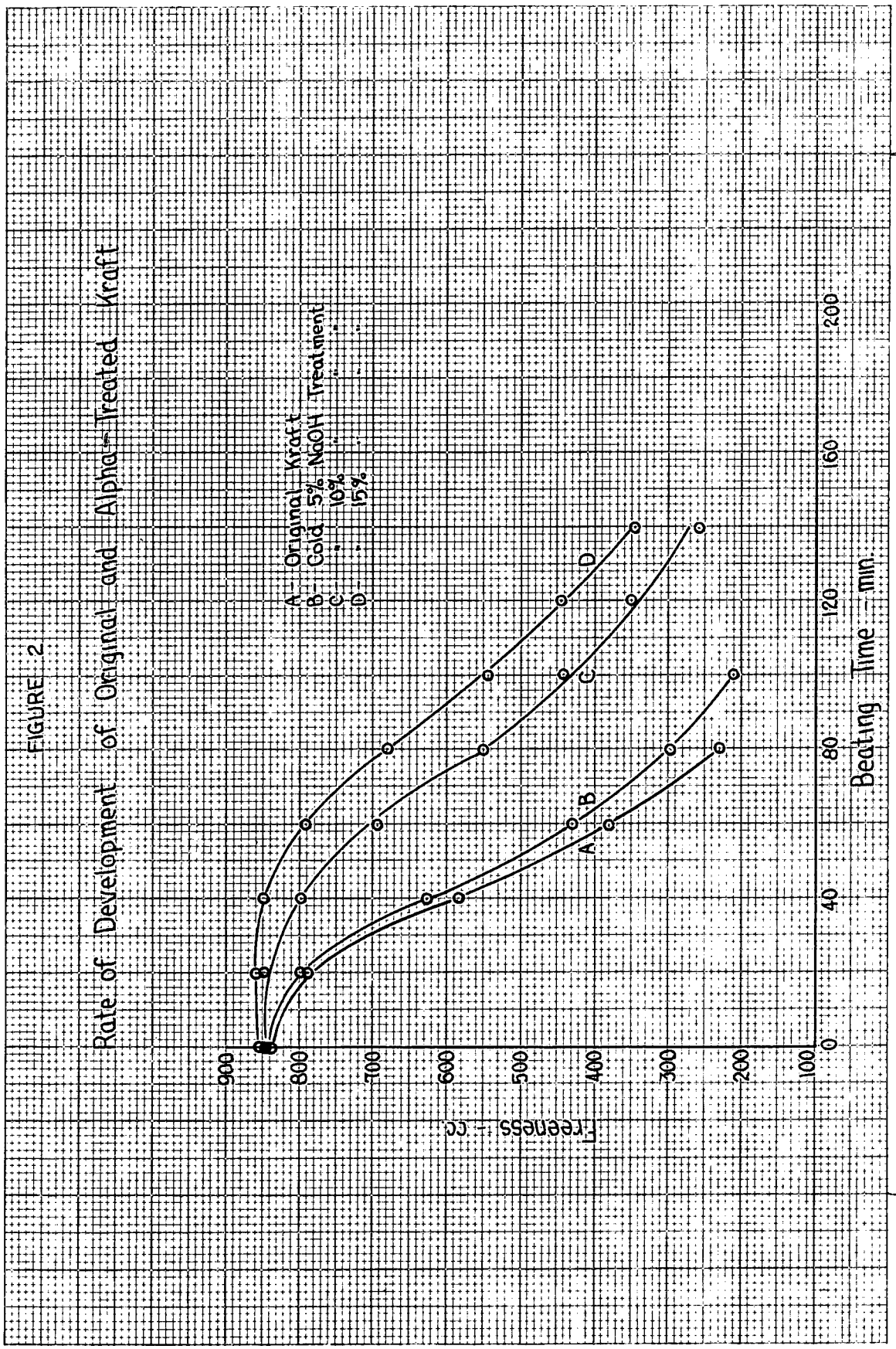


FIGURE 2
Rate of Development of Original and Alpha-Treated Kraft
A- Original Kraft
B- Cold 5% NaOH Treatment
C- " 10% " "
D- " 15% " "
Freeness - cc
900
800
700
600
500
400
300
200
100
0
40
80
120
160
200
Beating Time - min.
A
B
C
D

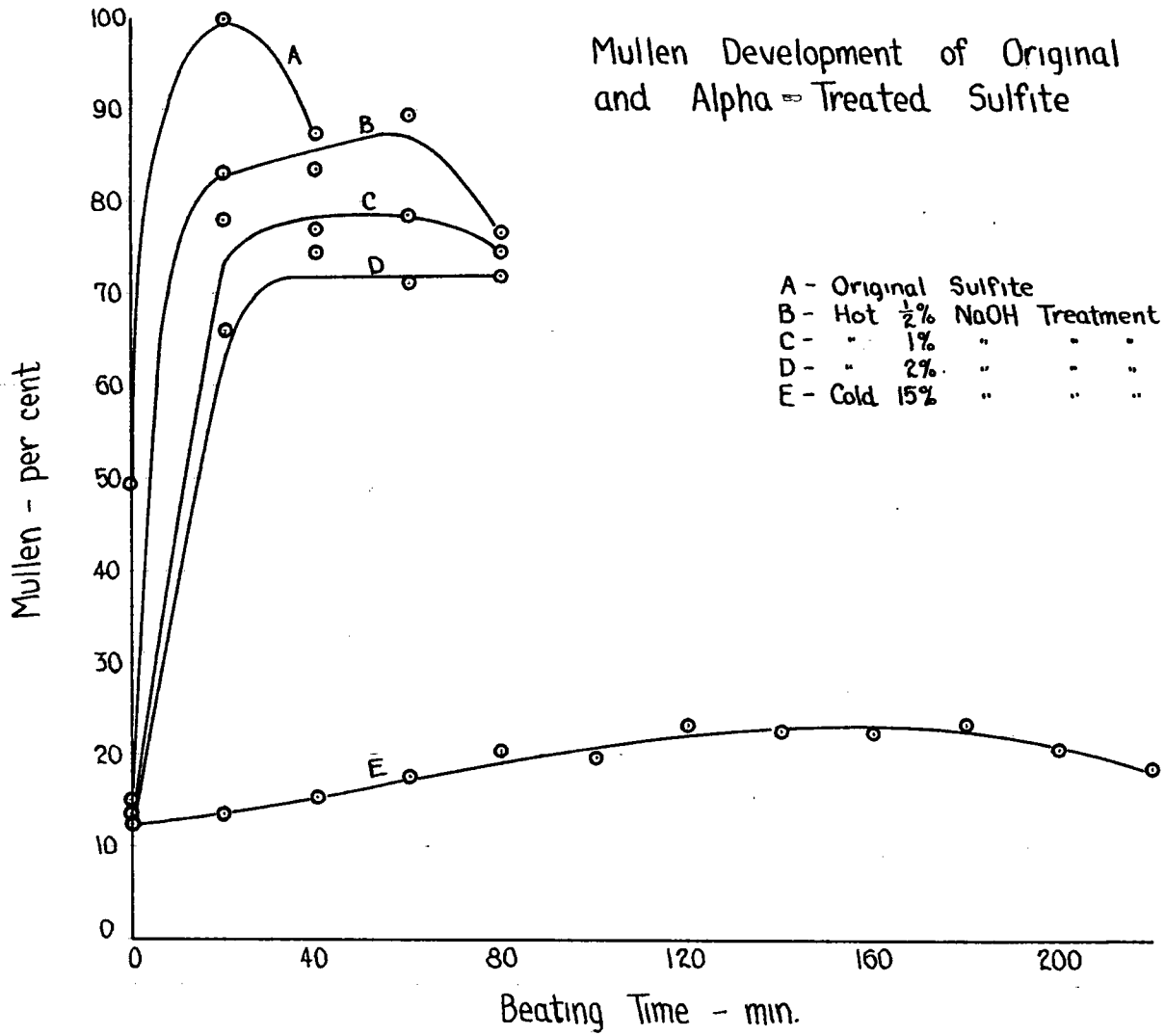
cold 15 per cent alkali-treated stock was extremely hard to hydrate. The data for the kraft pulps (Figure 2), which were subjected to cold sodium hydroxide treatments only, indicate that the 5 per cent-treated stock has not been lowered appreciably in rate of freeness drop, whereas the 10 and 15 per cent alkali-treated pulps show abnormally slow freeness lowering.

Figures 3 and 4 indicate the Mullen development. From Figure 3 it is seen that the hot treatment gives pulps of lower maximum Mullen, but the losses in strength are not excessive; the pulps require a somewhat longer period to develop this strength than the original pulp. The cold 15 per cent-treated pulp shows an extremely low Mullen with practically no development in strength. Figure 4 indicates that the 5 per cent-treated kraft has a lower maximum Mullen and takes slightly longer to develop than the original stock; the 10 and 15 per cent-treated krafts, however, show very great losses in the maximum Mullen and also show very slight development.

The fold data, as shown by Figures 5 and 6, should roughly parallel that of the Mullen. Here, however, the changes are greater because the test is more sensitive, and the results are more noticeable. Figure 5 shows that even the hot treatment lowers the fold considerably, whereas the cold 15 per cent sodium hydroxide-treated sulfite has no fold at all. Likewise, Figure 6 shows relatively small lowering of the fold values for the 5 per cent treatment but abnormal drops for both the 10 and 15 per cent-treated kraft pulps.

Figure 7 shows that the hot processed pulps do not decrease in tear as fast as the original pulp. This would be expected from the

FIGURE 3


Mullen Development of Original and Alpha - Treated Sulfite
A - Original Sulfite
B - Hot ½% NaOH Treatment
C - " 1% " " "
D - " 2% " " "
E - Cold 15% " " "
Mullen - per cent
Beating Time - min.
0
10
20
30
40
50
60
70
80
90
100
0
40
80
120
160
200
A
B
C
D
E

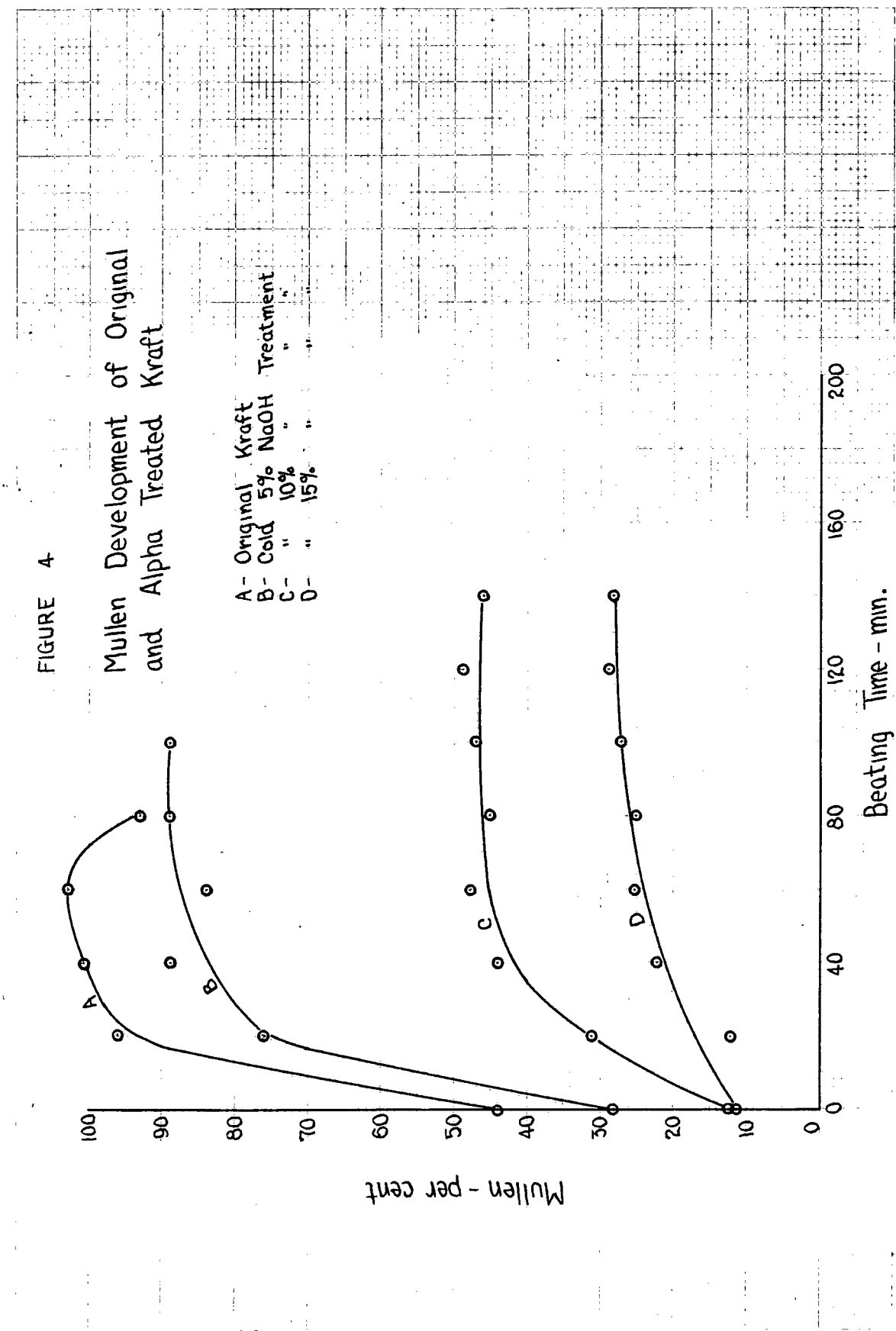


FIGURE 4

Mullen Development of Original and Alpha Treated Kraft

A- Original Kraft
B- Cold 5% NaOH Treatment
C- " 10% " "
D- " 15% " "

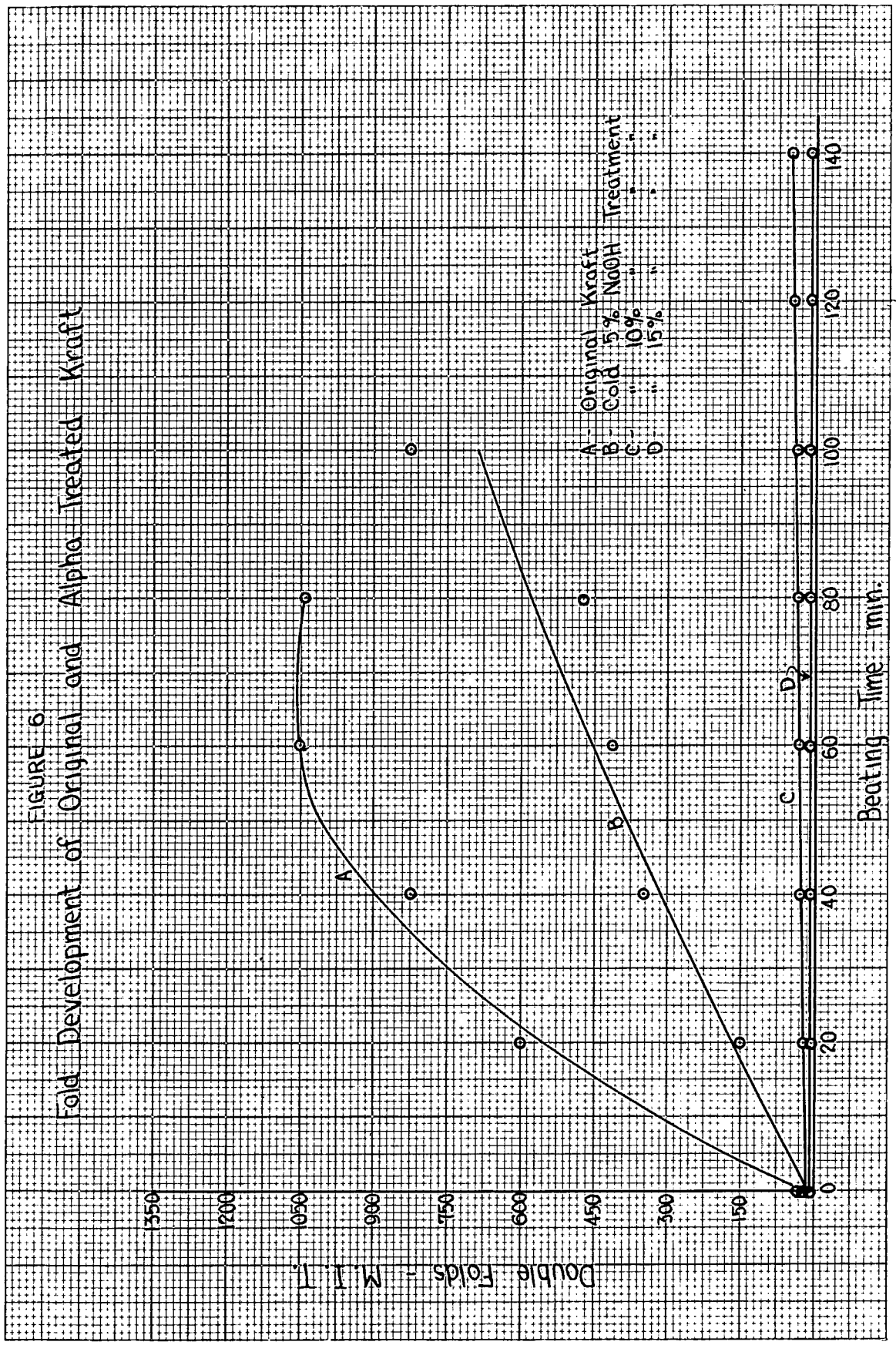
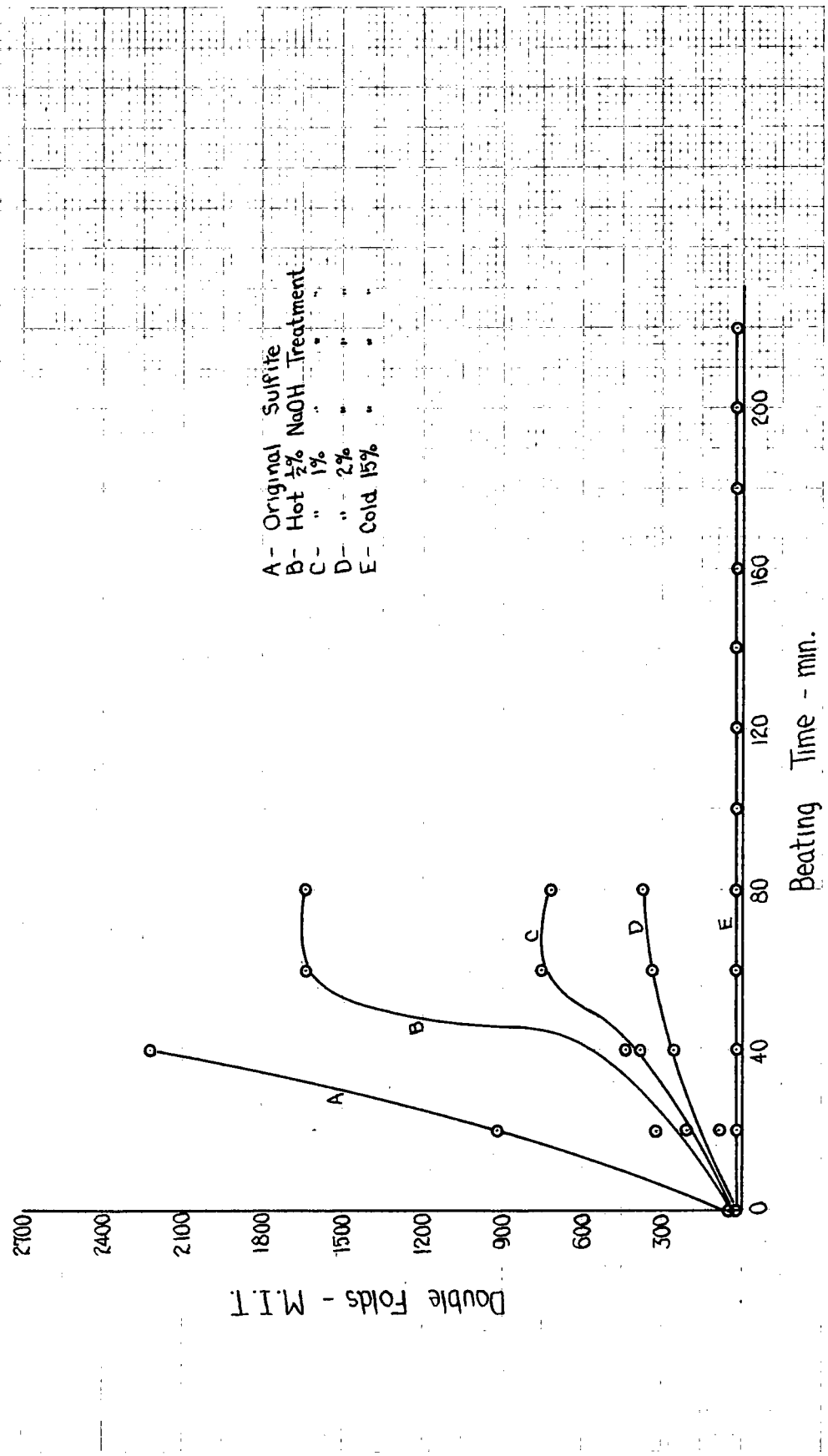


FIGURE 6
Fold Development of Original and Alpha Treated Kraft
Double Folds - M.I.T.
Beating Time - min.
A Original Kraft
B Cold 5% NaOH Treatment
C " " 10% " "
D " " 15% " "
A
B
C
D
0
20
40
60
80
100
120
140
150
300
450
600
750
900
1050
1200
1350

FIGURE 5

Fold Development of Original and Alpha Treated Sulfite



correspondingly lower rate of freeness drop and the Mullen and fold development. The 15 per cent-treated sulfite shows a general lowering in tear, but, from the peculiar shape of the curve, some other factor of great importance must have been operative, especially during the first 20 minutes of beating. After the beating had progressed somewhat, the effect of this factor evidently decreased, and the tear curve appears normal. This is attributed to two factors, "wild" formation and the tear test itself. In regard to formation, it was noticed that the sheets were rather wild for the unbeaten, 15 per cent-treated sulfite. This gives rise to peculiar tear curves and is encountered particularly on beating unbleached kraft pulps, for which the unbeaten sheets have poor formation. With such non-uniform sheets, the tear test is not very indicative, for this test depends on an integrated force applied over a relatively short line of tear; when the sheets tested are of uneven formation, the line of tear is usually very irregular and spurious results are obtained.

Figure 8 shows practically the same results. The 5 per cent alkali-treated kraft exhibits normal tendencies with the decrease in tear similar to and less rapid than that for the original kraft. The 10 and 15 per cent-treated samples have the same peculiar trends as the 15 per cent-treated sulfite.

The opacity change with beating is given in Figures 9 and 10. The former shows that the hot treatment slows up somewhat the rate at which opacity drops with beating; the original opacity of the hot treated sulfites, however, is fully 10 per cent higher than that of the original sulfite. The 15 per cent-treated sulfite shows a steady

FIGURE 7

Tear Change with Beating for Sulfite

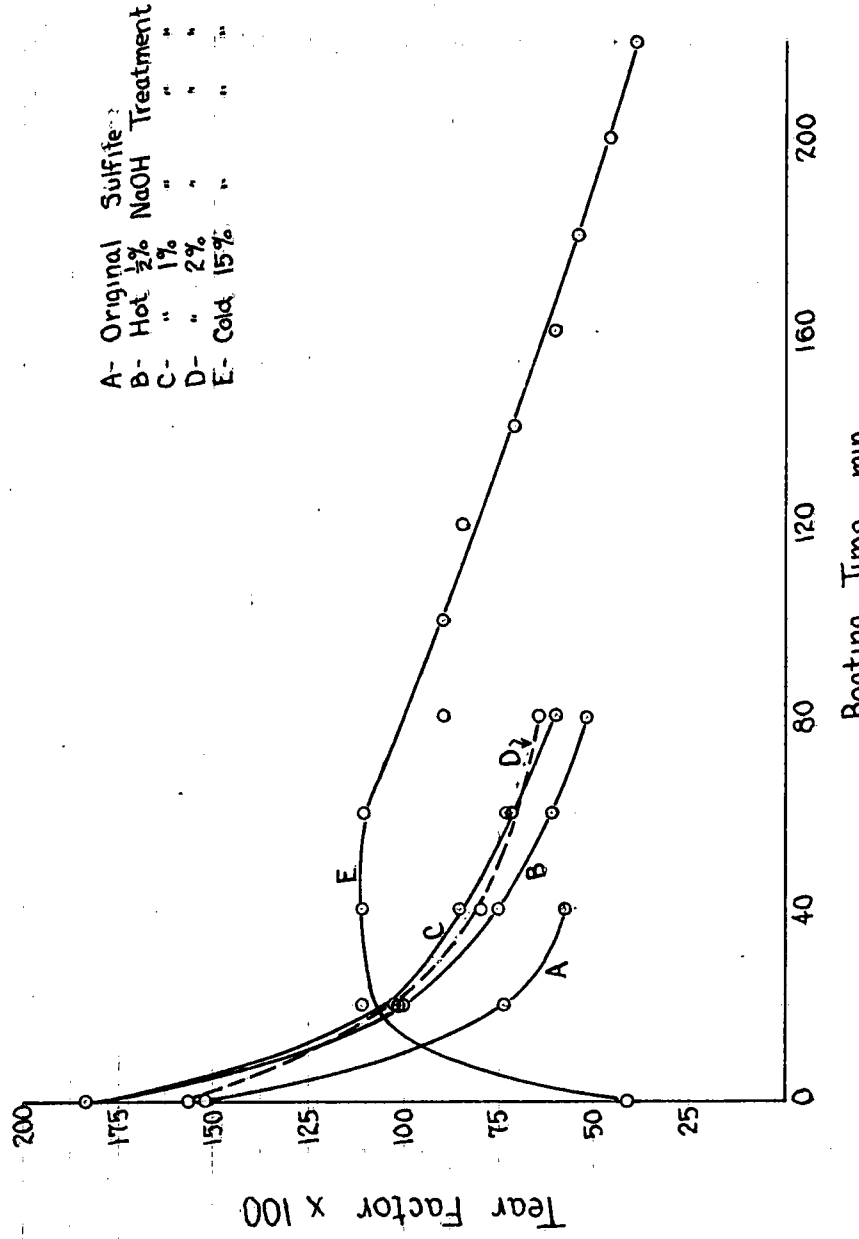
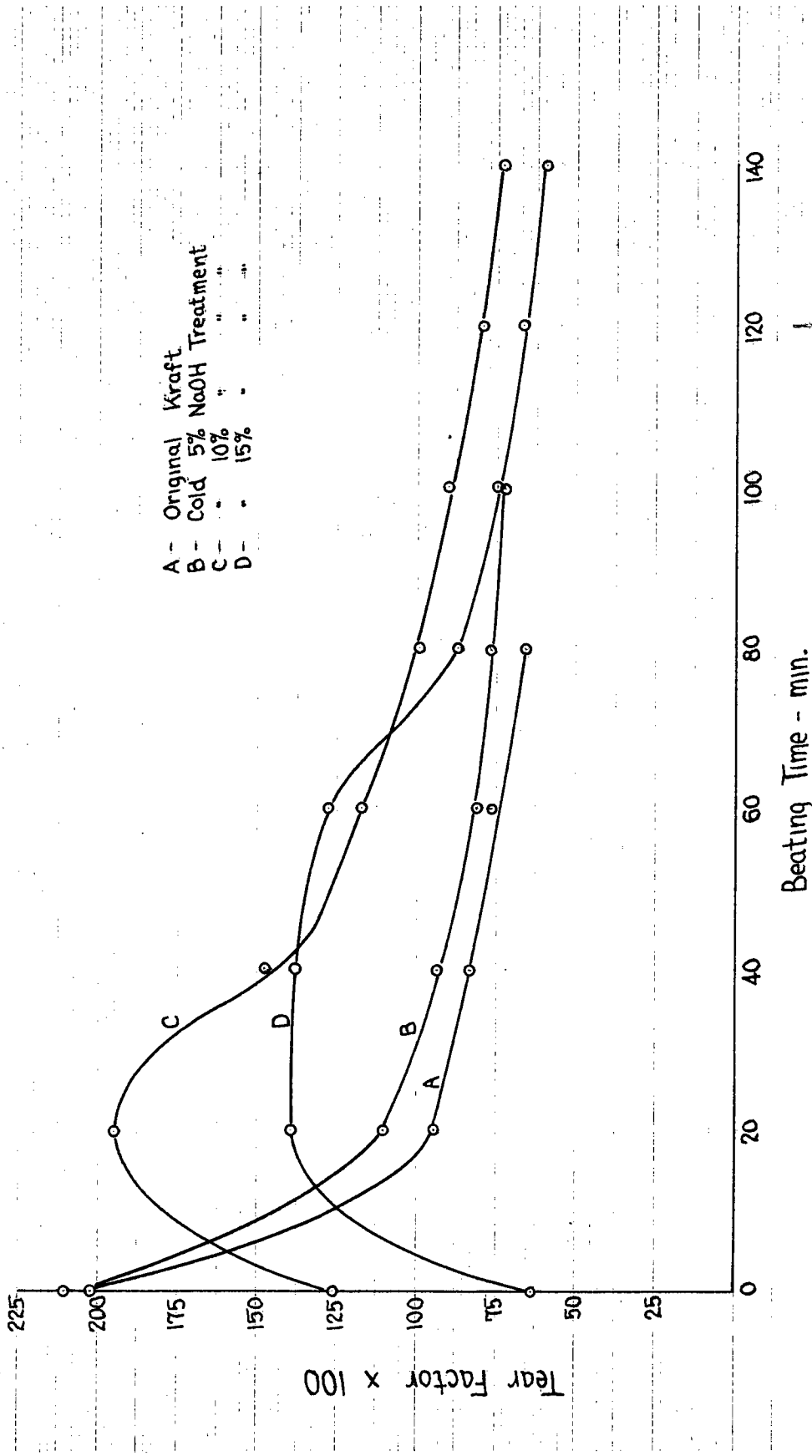


FIGURE 8

Tear Change with Beating for Kraft



increase in opacity on beating. This is definitely contrary to the action of normal pulp. As Figure 10 shows, the 5 per cent caustic soda-treated kraft reacts in the normal manner; in contrast, the 10 and 15 per cent treated krafts increase in opacity.

Thus, the study of the beating characteristics of the prepared wood pulps permits the following conclusions:

1. The hot process of alkaline purification results in a pulp which is slightly harder to beat, has somewhat lower Mullen and fold, and has a greater tear and opacity than the original pulp.
2. The 5 per cent cold sodium hydroxide treatment produces a pulp somewhat similar to that obtained from the hot process, i.e., slightly harder beating, lower Mullen and fold, but greater tear and opacity.
3. Pulps purified by treatment with cold 10 or 15 per cent sodium hydroxide have undergone radical changes. This is shown by abnormally long beating time, the development of extremely low Mullen, fold, and tear values, and the fact that the opacity increases on beating.
4. Since only pulps treated with 10 and 15 per cent caustic at 20° C. acted peculiarly, and judging from the fact that these concentrations of caustic at that temperature are known to mercerize cellulose, it was indicated that wood pulp cellulose that has been mercerized has greatly inferior papermaking properties.
5. In view of the above, the purification <u>treatment</u> and not the

FIGURE 9

Opacity Change with Beating for Sulfite

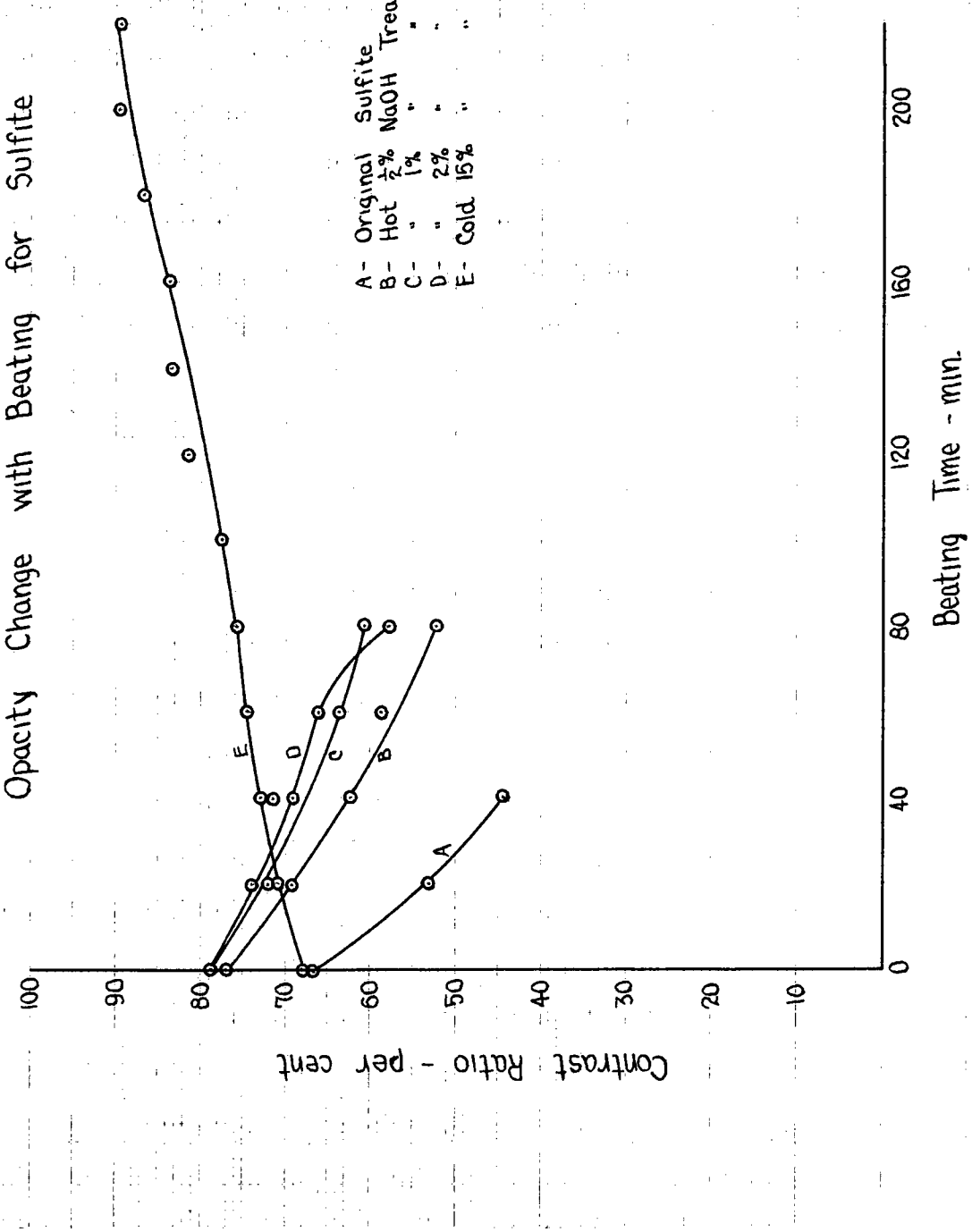
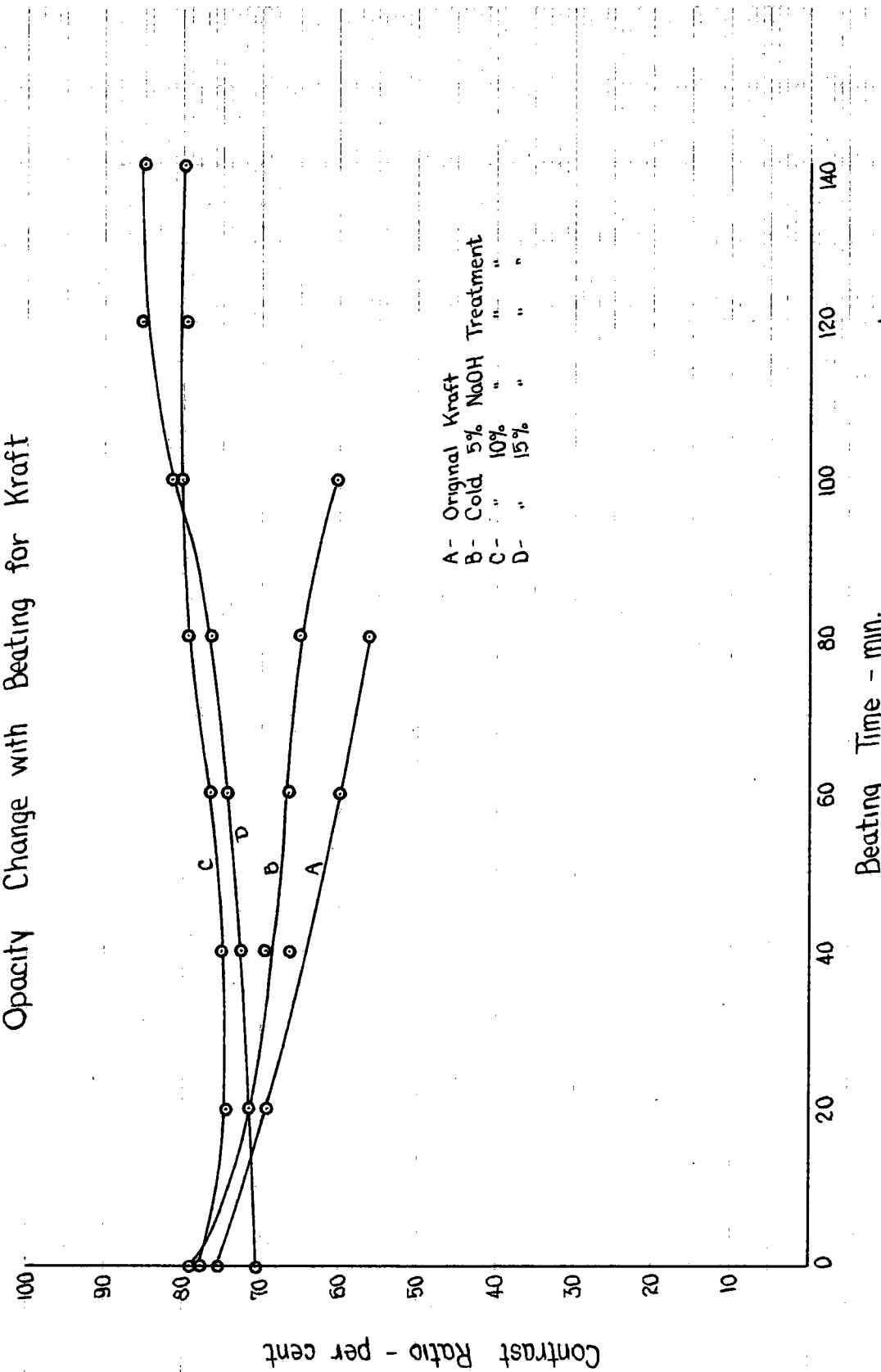


FIGURE 10

Opacity Change with Beating for Kraft



removal of materials, seems to be the governing factor in determining the papermaking properties of a purified pulp.

C. THE RELATION BETWEEN THE PHYSICAL CHARACTERISTICS AND CHEMICAL COMPONENTS OF PURIFIED PULPS

Table VI shows the physical characteristics of the various pulps evaluated at a freeness of 500 cc. Schopper-Riegler.

TABLE VI

EVALUATION OF WOOD PULPS AT 500 FREENESS

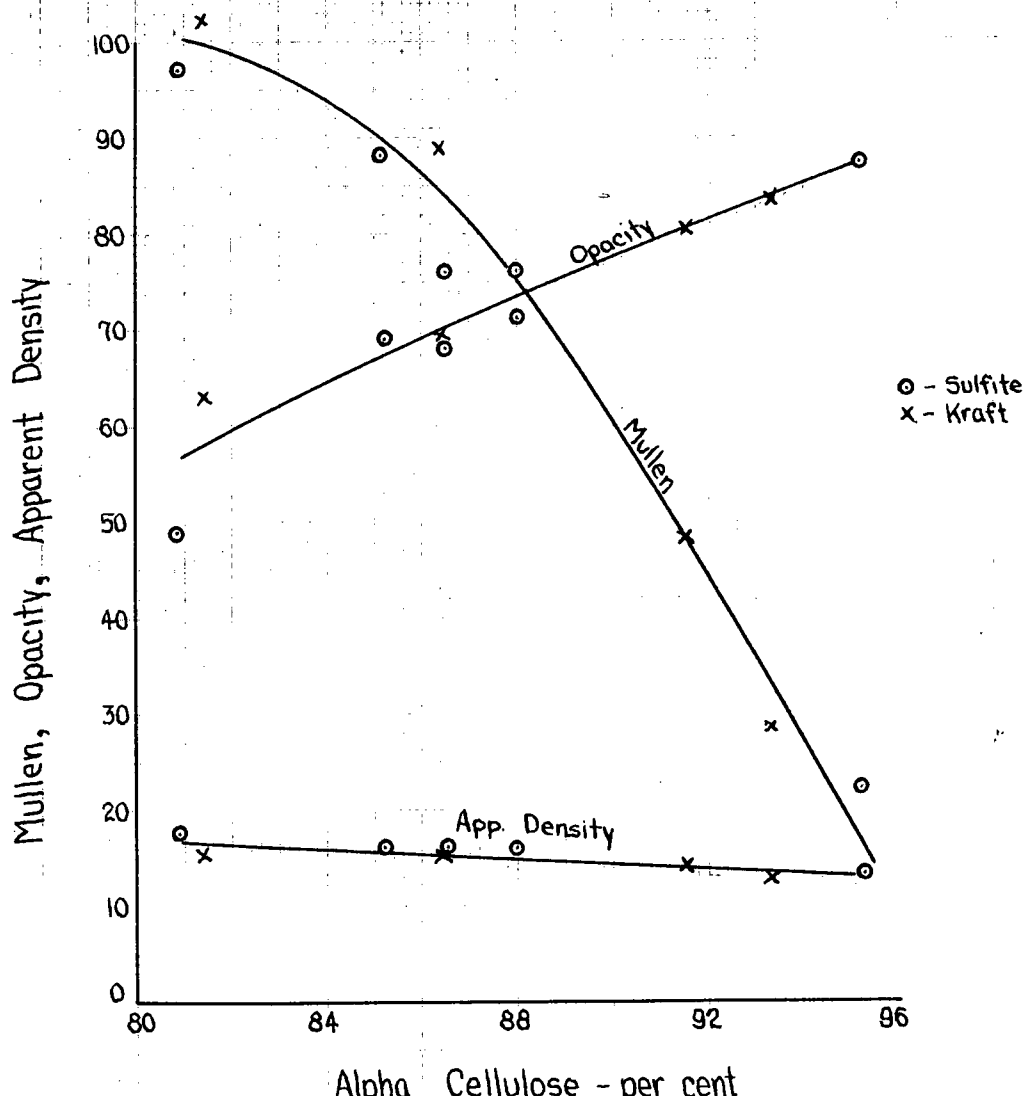
Pulp	Time to 500 Freeness min.	Mullen %	M.I.T. Fold	Tear Factor x 100	Apparent Density	Opacity
Original Sulfite	29	97	1480	66	17.5	49
Hot 1/2% Sulfite	35	88	410	79	16.0	69
Hot 1% Sulfite	36	76	340	88	16.0	68
Hot 2% Sulfite	37	76	240	85	16.0	71
Cold 15% Sulfite	176	22	2	55	13.0	87
Original Kraft	48	103	950	81	15.6	63
Cold 5% Kraft	53	89	400	84	15.2	69
Cold 10% Kraft	89	48	30	95	14.0	80
Cold 15% Kraft	115	28	7	71	12.5	83

These values were studied in relation to the chemical constants of the pulp (Table III, page 33). Figure 11 shows the results of plotting the opacity, apparent density, fold, and Mullen of the sulfite and kraft pulps against the alpha-cellulose content of the pulp. The alpha-cellulose value was selected because it was the only one in which there was even a remote relationship. Straight line relationships with alpha-cellulose appear for opacity and apparent density values; the opacity increases as the purity of the pulp increases, and the apparent density decreases. These relations result from the fact that with

FIGURE 11

Relation of Physical Properties to Alpha Cellulose

All physical properties at 500 Freeness



increased purity of the stock, there is a decreased fiber-to-fiber contact. This is borne out by the lowering of bursting strength.

Little correlation is noted for other analytical values. This supports the view outlined in the last section, that it is the process used in purification which controls the physical properties of the pulps produced rather than the removal of chemical components, and therefore there should be little or no correlation between the physical properties and chemical components when a series is studied containing pulps purified by a nonmercerizing process and pulps produced by a mercerizing process.

D. BEATING CHARACTERISTICS OF RAG STOCKS

The physical tests on rag stocks, as explained on page 25, do not permit direct comparison with those on wood pulps because a different beating procedure had to be used. Table VIII lists the rag stock beating data, while the following table gives the properties of the rag stocks evaluated at 350 cc. freeness to approximate commercial conditions:

TABLE VII

EVALUATION OF RAG STOCKS AT 350 FREENESS

Pulp	Time to 350 Freeness min.	Mullen %	Tear Factor x 100	M.I.T. Fold	Apparent Density	Opacity
Original Rag Stock	220	70	360	900	8.2	74
Hot 1/2% Rag	207	68	410	800	8.3	71
Hot 1% Rag	195	57	390	310	7.9	72
Hot 2% Rag	88	64	290	400	8.8	75
Cold 5% Rag	200	52	380	210	8.5	73
Cold 10% Rag	150	56	340	160	7.9	78
Cold 15% Rag	138	44	250	40	9.0	84

TABLE VIII

BEATING CHARACTERISTICS OF RAG STOCKS

Original Rag Stock

Time min.	Freeness cc.	Basis Weight 25x40-500	Caliper mils	Apparent Density	Mullen pts./#	Tear Factor	Opacity	M.I.T. Fold
210	360	43.0	5.4	8.0	65	3.7	75	800
240	300	42.8	5.0	8.5	81	3.3	72	1100
			Hot 1/2% NaOH-Treated Rag					
120	580	41.6	5.6	7.4	55	5.00	80	180
150	490	42.6	5.3	8.0	61	4.34	72	448
210	340	41.3	5.0	8.3	68	4.12	77	810
			Hot 1% NaOH-Treated Rag					
150	470	44.2	5.9	7.5	54	4.10	73	195
210	320	43.4	5.4	8.0	58	3.92	71	351
			Hot 2% NaOH-Treated Rag					
75	430	43.4	5.2	8.3	62	3.20	76	308
105	290	42.9	4.5	9.5	68	2.61	75	512
			Cold 5% NaOH-Treated Rag					
165	450	41.5	5.5	7.5	51	3.35	79	133
195	360	43.6	5.2	8.4	53	3.67	74	196
			Cold 10% NaOH-Treated Rag					
135	400	39.2	5.3	7.4	54	3.52	77	136
165	300	41.4	4.9	8.4	58	3.33	80	188
			Cold 15% NaOH-Treated Rag					
105	475	42.4	5.1	8.3	35	2.66	83	26
150	320	42.3	4.6	9.2	47	2.41	84	44

It should be noted that the time to develop 350 cc. freeness is shorter for the treated rag stocks than for the untreated, an observation which is directly opposite to the results with wood pulps. Why this is true has not been explained by the data on hand.

In agreement with the findings on wood pulps, the hot process does not lower the papermaking properties excessively, as shown by the Mullen, tear, and fold tests. Neither does the cold 5 per cent alkali treatment greatly influence these properties. The 10 and 15 per cent-treated rag stocks show somewhat greater losses, although the mercerized rag stocks do not show the almost complete loss in strength found with the mercerized wood pulps, largely because of the much greater fiber length of the rag stock. The opacity effects were similar to those found for wood pulps, i.e., the 10 and 15 per cent-treated stocks have their opacity increased on beating.

Thus, the experiments show that rag stocks also exhibit abnormal losses of papermaking properties whenever the treatment involves the use of 10 or 15 per cent sodium hydroxide. Actually, the chemical properties of the rag stocks were changed very little by the treatments, as the data in Table III show. However, Table VII shows that the papermaking properties varied considerably. The data indicate very clearly that the <u>treatment</u> is the important factor in determining the papermaking properties of the purified stock obtained, and that the materials removed are of secondary importance. Also, the data show that pulp which has been mercerized possesses inferior papermaking properties.

E. CUPRAMMONIUM SWELLING

Earlier work carried out at The Institute of Paper Chemistry and described by Carpenter and Lewis (69), and later illustrated by cinémicrographs by Olga Smith, have shown a relation between the treatments given fibers and their behavior with swelling agents. In particular, processes of degradation, such as overbleaching, overcooking, extended oven-drying, and acid degradation affect the resistance of pulp fibers to cuprammonium hydroxide, and the fiber no longer increases in size with the attendant formation of beads or larger sausage-shaped balloons, but rather dissolves without apparent swelling. When the degradation has been sufficiently severe, as was one case in which basswood had been treated with strong nitric acid and potassium chlorate, the primary wall of the fiber appeared to have been rendered so soluble in the swelling agent that the fibrils first fell apart in the cuprammonium solution and then disappeared. In contrast, commercial alpha pulp appeared to be somewhat more resistant to swelling, as indicated by the higher concentration of solution required for beading or ballooning.

This same technique was applied to the purified pulps, in order to determine what change, if any, could be noted in the behavior of the fibers treated by hot and cold and dilute and more concentrated alkaline solutions. The microscopic observations have been converted into numerical units which indicate the number of fibers in a field which have swelled, the number which have formed a chain of beads (Figure 13), the number which have swollen as sausage-like balloons (Figure 14), and the number which have dissolved.

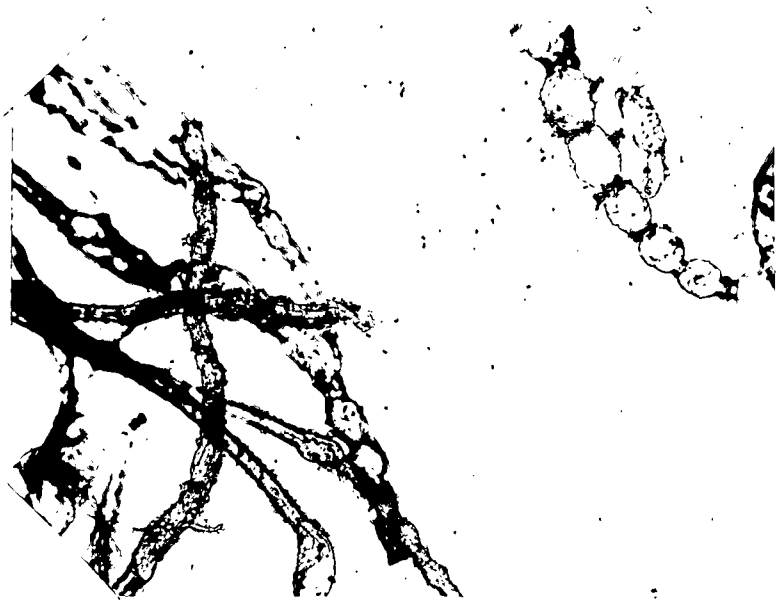


FIGURE 13

Illustration of a Beaded Fiber

FIGURE 14

Illustration of a Ballooned Fiber

The results are assembled in Table IX. It will be seen that wood pulps may bead or balloon by cuprammonium swelling, depending upon how they have been purified. All the mercerized wood pulps give beading and some ballooning, whereas those that have not been mercerized simply bead. This would indicate, again, that the treatment is an important factor in the swelling behavior. This conclusion is supported by the rag stock swelling data, because it is seen that the swelling characteristics of the different samples vary considerably. It has previously been shown, however, that the chemical properties are very much the same; thus, the important factor which characterizes the differences in the cuprammonium swelling behavior of fibers must be the type of treatment to which they have been subjected and not the degree of purity of the material.

The results also indicate that the kraft pulps were much harder to swell in cuprammonium than were the sulfite pulps. The kraft pulps did not swell in a bead-like or balloon-like manner, but the fiber swelled somewhat in the cuprammonium solution and then dissolved. The sulfite pulps, on the other hand, beaded before going into solution, and at a lower concentration of cuprammonium than for the kraft pulp.

F. SWELLING BEHAVIOR IN 17.5 PER CENT SODIUM HYDROXIDE

The results of swelling the pulps in 17.5 per cent sodium hydroxide are given in Table X.

The data show that for wood pulps the percentage of increase in weight is considerable, and the percentage of elongation is small

TABLE IX

SWELLING OF FIBERS IN CUPRAMMONIUM SOLUTIONS

Legend:

ss means slight swelling
s means swelling
b. means beaded
d. means dissolved
bl. means ballooned

Percentages are the per cent of all the fibers viewed.

		% Cuprammonium							
		25	30	35	40	45	50	55	60
Original Sulfite	b.	40%	15%	15%	8%				
	d.		30	70	90	95%			
Hot 1/2% Sulfite	b.	ss	50	40	18				
	d.		10	30	80	95			
Hot 1% Sulfite	b.	ss	50	60	15				
	d.			30	80	95			
Hot 2% Sulfite	b.		ss	40	70	40	15%	5%	
	d.				30	60	85	95	
Cold 15% Sulfite	b.		ss	ss	15	30	50	16	4%
	d.						20	80	95
	bl.					5	30	4	1
Original Kraft	b.	ss	2	4	8	8			
	d.					8	70	95	
Cold 5% Kraft	b.			ss	12	24	4		
	d.						90	95	
Cold 10% Kraft	b.			ss	4	8			
	d.					40	95		
	bl.					20			
Cold 15% Kraft	b.			ss	s	8	30	15	
	d.							75	95
	bl.						5	5	
Original Rag	d.		ss	ss				50	80
	bl.				80	95	95		
Hot 1/2% Rag	d.		ss	s			50	80	90
	bl.				80	95			
Hot 1% Rag	d.			ss	s		50	80	90
	bl.					90			
Hot 2% Rag	d.			ss	s		50	80	90
	bl.					80			
Cold 5% Rag	d.			ss	s		50	80	90
	bl.					80			
Cold 10% Rag	d.				ss	s			70
	bl.						80	90	
Cold 15% Rag	d.				ss	s			20
	bl.						70	80	

TABLE X

SWELLING BEHAVIOR IN 17.5 PER CENT CAUSTIC

Pulp	Weight Increase %	Elongation %	Swelling Volume cc./100 g.
Original Sulfite	555	266	5.27
Hot 1/2% Sulfite	460	209	5.00
Hot 1% Sulfite	460	162	4.86
Hot 2% Sulfite	460	181	4.94
Cold 15% Sulfite	655	151	5.84
Original Kraft	540	261	6.11
Cold 5% Kraft	550	231	6.04
Cold 10% Kraft	620	210	5.95
Cold 15% Kraft	690	179	6.12
Original Rag	440	167	5.77
Hot 1/2% Rag	440	177	5.91
Hot 1% Rag	425	160	5.65
Hot 2% Rag	430	160	6.15
Cold 5% Rag	440	177	5.92
Cold 10% Rag	440	182	5.95
Cold 15% Rag	Sheet could not be made		

for pulps that have been mercerized, i.e., treated with 10 per cent or more of sodium hydroxide. These data agree with those of Jayme (5). Thus, this swelling test shows that some very pronounced physical change has taken place in the case of the mercerized wood pulps.

The data for the rag stocks are rather uniform. Apparently this test is not sufficiently sensitive to detect the differences in the rag stocks. Two factors might account for this. In the first place, the surface of the unbeaten rag sheets made for the test was extremely rough, so that great inaccuracies in the elongation measurements were possible; then, too, it was noticed that the wood pulp discs did not change in diameter appreciably upon swelling, whereas the rag discs contracted considerably in diameter. Both these factors

would result in errors in the test with the rag stocks.

Here again the swelling behavior with 17.5 per cent sodium hydroxide of pulps purified with the caustic solutions of 10 and 15 per cent concentrations runs parallel to the differences on beating.

G. OPTICAL PROPERTIES

Handsheets made from 15 per cent caustic-treated sulfite pulp were used for this first series of investigations. The pulp had been beaten 20 and 220 minutes, and the sheets are therefore labeled 15S-20 and 15S-220 respectively.

Evaluations of the $\underline{k}$ and $\underline{S}$ values for these sheets are given in Table XI.

TABLE XI

VARIATION OF $\underline{k}$ (ABSORPTION COEFFICIENT) AND $\underline{S}$ (SCATTERING COEFFICIENT) VALUES WITH BEATING AND WITH WAVELENGTH

Sample	15S-20	15S-220	15S-20	15S-220	15S-20	15S-220	15S-20	15S-220
Wavelength	420		500		600		700	
R_0	62.7	62.9	63.8	65.2	63.4	66.4	63.1	66.4
$R_{.98}$	85.3	69.3	91.9	77.0	95.5	80.2	95.6	80.9
R_∞	75.2	65.7	82.5	71.0	88.5	73.5	76	74
Sx	2.02	3.2	1.93	2.67	1.78	2.68	2.0	2.68
$k/S \times 10^3$	40.9	89.5	18.6	59.2	7.5	47.8	37.9	45.6
$kx \times 10^3$	88.3	286	22.9	158	13.3	128	75.8	122
x	5.0	3.2	5.0	3.2	5.0	3.2	5.0	3.2
$k \times 10^3$	17.7	89	4.6	49.2	2.7	40.0	15.2	38.4
$S \times 10^3$	407	1000	386	834	356	835	400	840

First, these data show the variation of $\underline{k}$ and $\underline{S}$ with wavelength. In the extreme red and blue, the sheet absorbs more light than at wavelengths of 500 and 600 mmu. The scattering coefficient does

not vary greatly over the wavelength range shown.

Further, the value of k, the absorption coefficient, increases greatly with beating. For instance, the value of K at 600 mmu. increases by a factor of 15 when the time of beating is increased from 20 to 220 minutes. In other words, handsheets made from pulps increase in the amount of light absorbed as the time of beating increases. Since beating ordinarily results in increased sheet density, thereby requiring more fiber-to-fiber contacts, the fact that a thinner sheet should absorb more light seemed paradoxical. This would seem to be an interesting field for research at some future time.

The scattering coefficient of this pulp also increases on beating. At 600 mmu., the S value increased from 0.356 to 0.835. This result was to be expected because it was reflected in the increased opacity on beating.

The absorption coefficient increase might be due to materials picked up from the beater or possibly to materials adsorbed from the water used in beating. To test this, samples of the original sulfite stock beaten for 40 minutes and unbeaten were compared with samples of the 15 per cent-treated pulp beaten for 40 minutes and unbeaten. The amount of foreign material adsorbed should have been approximately the same. Since the original sulfite beats down to 275 cc. freeness in 40 minutes, this short beating time indicated whether the k increase shown in the above table was spurious or not.

It is seen from the data in Table XII that beating lowered the scattering coefficient and the opacity of normal pulps; for the

TABLE XII

EFFECT OF BEATING ON THE k AND S VALUES

Wavelength 600 mmu.

	0S-0	0S-40	15S-0	15S-40
R_0	60.9	31.2	61.8	64.0
$R_{.98}$	93.9	70.0	95.8	94.1
R_∞	85	45	88.5	85
Sx	1.63	0.65	1.66	1.89
$k/S \times 10^3$	13.2	33.6	7.5	13.2
$kx \times 10^3$	21.5	21.8	12.5	25
x	3.5	2.5	5.8	4.5
$k \times 10^3$	6.15	87.1	2.16	5.55
$S \times 10^3$	466	260	286	420

15 per cent-treated pulp, the scattering coefficient and the opacity increased with beating. In other words, this pulp must have been changed very fundamentally.

In addition, the increase in absorption coefficient on beating is validated. The untreated sulfite shows an increase in k by a factor of 14; thus, the increase of k on beating must be a fundamental property of beaten pulps.

Since beating increases the sheet density, the question naturally arises whether calendering, which also increases the sheet density, will increase the k value. Table XIII, which represents the data obtained upon the calendering of a sheet of the original unbeaten sulfite, shows that even calendering effects an increase in the absorption coefficient of a sheet. This is surprising in that for sheets of higher density with more fiber-to-fiber interfaces, and fewer fiber-to-air interfaces, the absorption of light is greater.

TABLE XIII

EFFECT OF CALENDERING UPON THE k AND S VALUES

Wavelength 600 mmu.

	Uncalendered OS-0	Calendered OS-0
Opacity	65	59
R_0	60.9	54.1
$R_{.98}$	93.9	91.7
R_∞	85	78
Sx	1.63	1.2
$k/S \times 10^3$	13.2	31
$kx \times 10^3$	21.5	37.2
x	3.5	2.1
$k \times 10^3$	6.15	17.7

The absolute reflectances and transmittances of several samples were then determined on the General Electric recording spectrophotometer. The difference of the sum of the reflectance and transmittance from 100 per cent is the amount of light absorbed by the sheet. These data are given in Table XIV.

TABLE XIV

ABSOLUTE METHOD OF DETERMINING THE ABSORPTION OF A SHEET

Wavelength 600 mmu.

	Uncal. OS-0	Cal. OS-0	OS-0	OS-40	Uncal. Glassine	Cal. Glassine
Reflectance %	59.0	55.5	58.3	28.7	23.6	18.9
Transmittance %	37.9	38.2	39.1	52.7	67.9	71.2
Absorption %	3.1	6.3	2.6	18.6	8.5	9.9

It is shown that whenever the sheet structure is made more dense, the absorption of light increases, whether the change has been caused by beating or by calendering.

Unbeaten original kraft (OK-0), original kraft beaten 80 minutes (OK-80), unbeaten 15 per cent-treated kraft (15K-0), and 15 per cent-treated kraft beaten 80 and 140 minutes (15K-80, 15K-140) were then investigated to see whether the results apply to kraft. Table XV shows that the conclusions drawn for sulfite pulp hold also for kraft pulps. This may be diagrammed as:

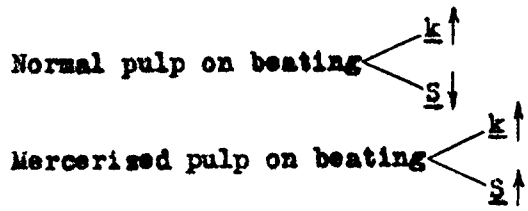


TABLE XV

DETERMINATION OF THE k AND S VALUES FOR TREATED KRAFT SHEETS

Wavelength 600 mmu.

	OK-0	OK-80	15K-0	15K-80	15K-140
R_0	66.5	42.0	64.5	66.7	68.0
$R_{.98}$	91.7	82.5	93.7	88.6	79.1
R_∞	83	62.5	85	80.2	73.5
Transmittance	30.7	45.2	33.3	25.5	20.0
Absorption	2.8	12.8	2.2	7.8	12.0
$k/S \times 10^3$	17.4	113	13.2	24.4	47.8
Sx	2.18	0.86	1.93	2.27	3.10
x	4.0	2.8	7.0	4.1	3.5
$S \times 10^3$	545	307	276	553	885
$k \times 10^3$	9.5	34.8	3.6	14.1	42.3

To eliminate the possibility that materials might be absorbed from the water so that k is increased on beating, two samples of the original sulfite were treated as follows: One was stirred for 220 minutes (which was the longest beating time of any of the beaten pulps) using an amount of water equivalent to that of the beating procedure. This sample was labeled Sheet 2. Sheet 1 was simply made from the

original sulfite. It was reasoned that if coloring materials were being absorbed from the water, Sheet 2 should have a greater k than Sheet 1. In addition, the 10 per cent treated kraft and the original and 15 per cent alkali-treated rag samples were investigated.

TABLE XVI

k AND S VALUES OF VARIOUS SHEETS

Wavelength 600 mmu.

	Sheet 1	Sheet 2	10K-0	10K-140	0R-210	0R-240	15R-105	15R-150
R_0	62.7	63.1	69.6	63.2	64.5	64.5	65.1	67.0
$R_{.98}$	97.1	96.9	94.0	82.1	91.2	89.6	85.9	87.9
R_∞	92.5	92.5	87	73.5	82	80	77	79
$k/S \times 10^3$	3.04	3.04	9.71	47.8	19.8	25	34.4	27.9
Sx	1.68	1.70	2.45	2.10	2.0	2.05	2.20	2.38
x	5.8	5.8	5.5	3.0	5.4	5.0	5.1	4.6
$S \times 10^3$	290	293	445	700	370	410	430	517
$k \times 10^3$	0.88	0.89	4.32	33.4	7.34	10.2	14.8	14.5

The following conclusions were drawn from data presented in Table XVI:

1. The absorption coefficient for pulps does not increase with beating because of materials absorbed from the water. The data for Sheets 1 and 2 prove this.
2. The fact that the 10 per cent alkali-treated kraft samples have been mercerized in the purification process is again shown by the fact that the scattering coefficient increases on beating.
3. The absorption coefficient for rag stocks increases with beating. The increases shown in Table XVI are not very large because the beating time between samples on the rag sheets is short (about 30 minutes).
4. The 15 per cent sodium hydroxide-treated rag stock shows

an increase in scattering coefficient with beating because of the mercerization effects.

To ascertain whether material from the bedplate was being worn off to cause the increase in k with beating, a sample of commercial bleached sulfite was beaten with the usual methods; a second sample was just slushed in the beater for the same length of time without weight on the bedplate. Also, a commercial papermaking alpha pulp was beaten to determine how it would behave. The data tabulated in Table XVII show that it is not material from the bedplate and roll which causes the absorption coefficient to increase with beating, but it is a fundamental property of sheets of higher density, assuming that material ground off the beater case in beating is about the same as that worn off by slushing.

TABLE XVII

DETERMINATION OF THE EFFECT OF MATERIAL FROM THE BEDPLATE ON BEATING AND THE ACTION OF A COMMERCIAL ALPHA PULP

Wavelength 600 mmu.

	Slushed 0'	Slushed 45'	Beaten 0'	Beaten 45'	Alpha 0'	Alpha 60'
R_0	73.2	73.1	74.2	54.3	71.5	56.0
$R_{.98}$	95.3	95.1	95.5	85.9	94.1	89.1
R_∞	91	91	91	72.5	88.0	76.0
$k/S \times 10^3$	4.45	4.45	4.45	52.2	8.2	37.9
Sx	2.82	2.82	3.0	1.36	2.7	1.42
x	5.0	4.9	5.0	3.0	5.5	3.2
$S \times 10^3$	564	575	600	453	490	445
$k \times 10^3$	2.51	2.56	2.66	23.6	4.0	16.9

The commercial papermaking alpha pulp investigated showed an increased absorption coefficient and only a slight decrease

in the scattering coefficient with beating. Thus, this pulp must be near the point where the scattering coefficient starts to increase with beating, and this fact would indicate a strong alkaline treatment in its preparation, but a treatment not quite sufficient in concentration to mercerize it.

This entire section, then, has demonstrated that pulps which have been mercerized in the purification treatment are much different from normal pulp in regard to the type of sheet formed.

In addition, and not directly applicable to the problem, it has been shown that with increased sheet density of normal or mercerized pulps, the amount of light absorbed by a sheet is increased. This fact has direct application to sheet blackening on calendering and may be of great interest to the manufacturers of glassine sheets. Further work should be done on these findings, but since such work is not directly important to the problem at hand, the finding is merely reported and has not been expanded. It is of interest that Foote (63) in his thesis, page 49, found the k value increased with beating. The finding was observed and reported, but was not stressed.

H. EQUILIBRIUM MOISTURE OF HANDSHEETS

So far, it has been shown that pulps given purification treatments in which a sodium hydroxide concentration of 10 per cent or greater is used produce a pulp of low papermaking qualities. This fact has been proved by data on the ease of beating, by strength tests, optical data on sheets, and actual swelling of the fibers with suitable agents. These results have been attributed to the fact that the

pulp was mercerized during the treatment, and that a changed form of cellulose was obtained. This changed form has been shown in the Historical Survey to be chemically identical with normal cellulose, but it exhibits increased hygroscopicity, increased dye absorption, and greater reactivity than the original material. Therefore, the hygroscopicities of the pulps were evaluated by determining the equilibrium moisture of the pulps at 65 per cent relative humidity and 70° F. The results are shown in Table XVIII.

TABLE XVIII

EQUILIBRIUM MOISTURE OF HANDSHEETS

Pulp	Water %	Pulp	Water %
Original Sulfite	9.73	Original Rag	8.27
Hot 1/2% Sulfite	9.19	Hot 1/2% Rag	8.36
Hot 1% Sulfite	9.11	Hot 1% Rag	8.46
Hot 2% Sulfite	9.18	Hot 2% Rag	8.38
Cold 15% Sulfite	11.17	Cold 5% Rag	8.37
		Cold 10% Rag	9.54
Original Kraft	9.34	Cold 15% Rag	10.89
Cold 5% Kraft	9.30		
Cold 10% Kraft	10.21		
Cold 15% Kraft	11.48		

It is clearly seen that upon merely purifying wood pulps with dilute hot caustic soda solution, the hygroscopicities change little; however, when a sodium hydroxide concentration of 10 per cent or greater is used, the hygroscopicities increase markedly. The rag stocks behave similarly. This indicates still further the fact that the effects already noted are due to this physical change in the cellulose on mercerization.

I. EFFECT OF RELATIVE HUMIDITY CHANGES ON FIBER WIDTH

Heretofore the results have shown that, as the pulps are purified with hot dilute caustic solutions, they lose some papermaking qualities and become very slightly less hygroscopic, excluding, of course, the mercerized pulps. It was therefore thought that perhaps any sodium hydroxide treatment makes the cellulose gel less reversible in nature and by that to explain somewhat the loss in papermaking properties. Since this irreversibility of the gel shows up very well in the degree of hysteresis shown by fiber width-relative humidity curves, the following data were obtained.

TABLE XIX

FIBER WIDTHS AT VARIOUS HUMIDITIES IN MICRONS

	Relative Humidity--Per Cent								
	95	58	0	58	95	58	0	58	95
Original Sulfite	37.8	36.5	34.6	35.8	36.6	36.1	34.6	35.5	35.9
Hot 2% Sulfite	36.1	34.9	32.9	34.2	34.9	34.6	32.9	33.8	34.3
Cold 15% Sulfite	22.8	21.8	20.1	21.0	21.8	21.2	20.1	21.0	21.6
Original Kraft	45.5	44.2	43.0	43.9	44.7	43.9	43.0	43.9	44.7
Cold 15% Kraft	24.4	23.3	21.6	22.5	23.4	22.5	21.6	22.5	23.3
Original Rag	22.9	21.8	20.4	21.4	22.4	21.5	20.4	21.4	21.8
Hot 2% Rag	24.0	22.8	21.1	22.2	23.2	22.3	21.1	21.9	22.7
Cold 15% Rag	24.3	23.0	21.2	22.4	23.3	22.5	21.2	22.1	22.8

Typical hysteresis curves were obtained, as Figure 12 and Table XIX show.

Table XX gives the results of calculating the percentage of change due to definite humidity changes.

FIGURE 12

Hysteresis of Original Sulfite

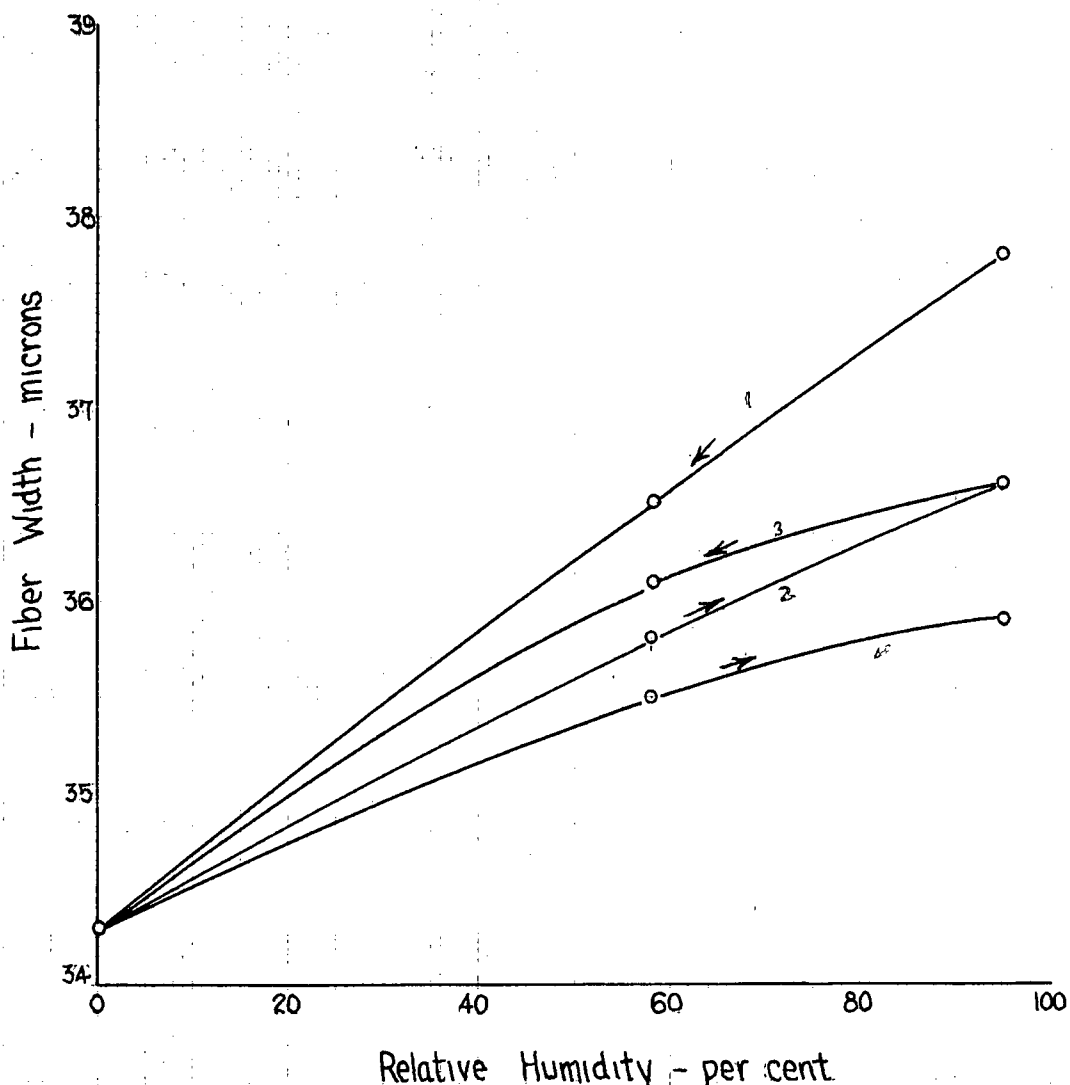


TABLE XX

PERCENTAGE OF CHANGE OF FIBER WIDTH WITH RELATIVE HUMIDITY CHANGES BASED ON THE WIDTH AT ZERO RELATIVE HUMIDITY

Legend:

1 - Humidity change 95% to 58% first cycle
2 - Humidity change 58% to 0% first cycle
3 - Humidity change 0% to 58% first cycle
4 - Humidity change 58% to 95% first cycle
5 - Humidity change 95% to 58% second cycle
6 - Humidity change 58% to 0% second cycle
7 - Humidity change 0% to 58% second cycle
8 - Humidity change 58% to 95% second cycle
T - Total per cent change over any humidity range
D-1 - Difference in per cent over first cycle
D-2 - Difference in per cent over second cycle

	1	2	T	3	4	T	5	6	T	7	8	T	D-1	D-2
Original Sulfite	3.8	5.5	9.3	3.5	3.5	7.0	1.4	4.3	5.7	2.6	1.2	3.8	2.3	1.9
Hot 2% Sulfite	3.6	6.1	9.7	4.0	2.1	6.1	0.9	5.2	5.1	2.7	1.5	4.2	3.6	1.9
Cold 15% Sulfite	5.0	8.5	13.5	4.5	4.0	8.5	3.0	5.5	8.5	4.5	3.0	7.5	5.0	1.0
Original Kraft	3.0	2.8	5.8	2.1	1.9	4.0	1.9	2.1	4.0	2.1	1.9	4.0	1.8	0.0
Cold 15% Kraft	5.1	7.9	13.0	4.2	4.2	8.4	4.2	4.2	8.4	4.2	3.7	7.9	4.6	0.5
Original Rag	5.4	6.9	12.3	4.9	4.9	9.8	4.4	5.4	9.8	4.9	2.0	6.9	2.5	2.9
Hot 2% Rag	5.7	8.1	13.8	5.2	4.7	9.9	4.3	5.7	10.0	3.8	3.8	7.6	3.9	2.4

These data show that in every case the loss in reversibility over the first complete cycle was greater for purified pulps, with the mercerized cellulose showing an even greater irreversibility than those purified with the nonmercerizing caustic. The method used, however, was insufficiently accurate to permit conclusions to be drawn on the second complete cycle. The changes encountered on the second cycle were of the order of magnitude of the probable errors in measurement, which explains why the results on the second cycle are obviously in error.

The large losses in papermaking properties cannot be blamed upon the irreversibility of the cellulose gel, although a tendency to become less reversible upon purification is shown. Once more, it is seen, especially from the rag stock data, that the purity is not the major factor, but that it must be the type of treatment which governs the papermaking properties of alpha-treated pulps.

J. EFFECTIVE CAPILLARY SIZE OF HANDSHEETS

The fact that sheets made from the regenerated pulps differ greatly from ordinary pulps has been shown before. To further emphasize this fact, the effective capillary diameter of handsheets was calculated.

The original data are given in Table XXI. The summarized results are given in Table XXII.

The slope n is the slope of the straight line of the log height of rise versus log time relation, as explained before. This is in good agreement with the theoretical value of 0.5. The k value

TABLE XXI

CAPILLARY RISE OF WATER IN SHEETS

The figures are the height of rise in millimeters of the water in the strip.

	Caliper mils	Time--Minutes 1	2	3	4	5	6	8	10
Original Sulfite	4.2	15	22	28	32	36	39	44	49
		16	23	29	33	37	40	45	50
		17	24	30	34	38	41	46	51
		16	23	29	33	37	40	45	50
		16	23	29	33	37	40	45	50
Average		16	23	29	33	37	40	45	50
Hot 2% on Sulfite	4.2	20	28	34	39	43	47	53	58
		19	26	34	39	44	48	56	63
		20	29	35	40	45	49	57	64
		20	29	35	40	45	49	57	64
		20	29	35	40	45	49	57	64
Average		20	29	35	40	45	49	57	64
Original Kraft	5.2	21	30	37	43	48	53	61	68
		22	31	37	43	48	53	61	68
		21	30	36	42	47	52	60	67
		22	31	37	43	48	53	61	68
		21	30	37	43	48	53	61	68
Average		21	30	37	43	48	53	61	68

		Time--Seconds 15	30	45	60	75
Cold 15% NaOH on Sulfite	10	38	57	68	78	85
		38	57	68	78	85
		40	59	70	79	86
		39	58	69	79	86
		39	58	69	79	86
Average		39	58	69	79	86
Cold 15% NaOH on Kraft	9.3	38	54	64	71	79
		39	55	66	75	82
		39	55	65	73	81
		39	55	66	74	82
		39	55	66	75	82
Average		39	55	66	75	81

TABLE XXII

EFFECTIVE CAPILLARY DIAMETER OF HANDSHEETS

	Slope n	k	Effective Diameter Microns	Caliper mils
Original Sulfite	0.492	2.92	16.1	4.2
Hot 2% Sulfite	0.510	3.50	19.3	4.2
Cold 15% Sulfite	0.515	61.25	338	10
Original Kraft	0.508	4.0	22.1	5.2
Cold 15% Kraft	0.470	97.0	535	9.3

was obtained from the actual data by applying the equation:

$$k = (h)^{\frac{1}{n}}/t.$$

The effective capillary diameter (D) was calculated from this k value by the equation:

$$D = 4kn/S \text{ (see page 31).}$$

The rag stocks were not investigated because the sheets formed from the unbeaten rag stocks were of poor formation and uniformity as would be expected.

These data show that the hot process apparently does not change the sheet structure appreciably as is evidenced by practically the same effective capillary diameter as was found in the sheets from the original untreated pulps. On the other hand, mercerized celluloses form sheets which act as though their effective capillary diameter has been increased by a factor of 20. This, together with the increased caliper of these sheets, shows that the fiber-fiber bonds must be considerably less in sheets from mercerized cellulose.

The effect of pressing the sheets of mercerized pulp was then determined. Sheets of the 15 per cent alkali-treated sulfite were made up and pressed at different pressures. The results are given in Table XXIII and summarized in Table XXIV.

TABLE XXIII

EFFECT OF PRESSING ON THE RATE OF CAPILLARY RISE IN SHEETS OF 15 PER CENT ALKALI-TREATED SULFITE

The figures are the height of rise in millimeters of the water in the strip.

Pressure #/sq. in.	Caliper mils	Time--Seconds 15	30	45	60	75	90
50	11	42	58	70	80		
		43	58	71	80		
		42	58	70	80		
		41	57	69	59		
		42	58	70	80		
Average		42	58	70	80		
75	8.5	41	56	68	76		
		40	54	66	74		
		42	57	69	77		
		42	57	69	77		
		41	56	68	76		
Average		41	56	68	76		
150	7.0	31	43	54	62	69	75
		33	45	56	64	71	78
		30	42	53	61	68	74
		30	41	53	61	68	74
		31	43	54	62	69	75
Average		31	43	54	62	69	75
300	5.5	27	38	47	53	60	64
		29	41	48	55	61	66
		27	39	47	54	60	66
		26	38	46	53	59	64
		26	39	47	54	60	65
Average		27	39	47	54	60	65

TABLE XXIV

EFFECT OF PRESSING ON THE CAPILLARY STRUCTURE OF HANDSHEETS MADE FROM COLD 15% CAUSTIC PURIFIED SULFITE PULP

Pressure #/sq. in.	Caliper mils	Slope n	k	Effective Capillary Diameter Microns
50	11.0	0.48	66.5	367
75	8.5	0.48	60.0	332
150	7.0	0.50	38.0	210
300	5.5	0.50	28.8	159

Thus, pressure can artifically cause fiber-to-fiber bonds as shown by the decreased effective capillary diameter and decreased caliper. The 15 per cent-treated stock pressed at 300 pounds per square inch resulted in a caliper of 5.5 mils and an effective capillary diameter of 159 microns, while the original sulfite pressed at 50 pounds per square inch gave a caliper of 4.2 and an effective capillary diameter of 16.1. In other words, even at approximately the same caliper, sheets of the regenerated pulps have approximately 10 times the effective capillary diameter of the normal pulp sheets. It is known that when fibers are mercerized and then washed, the fibers resulting are shrunken, twisted, and misshapen. This will be seen in a later section. It seems logical that with such fibers, a sheet must have fewer fiber-to-fiber bonds. The above capillary diameter data have shown this.

K. MULTISTAGE COOKING

The entire work up to this point has proved that the loss of papermaking qualities by pulps purified with mercerizing solutions is due to the type of treatment given the pulp in the purification

process. If these results are correct, it should be possible to subject a wood pulp to successive hot treatments of low concentration alkali, and a highly purified pulp of good papermaking properties should result.

The equivalent of 4 pounds of oven-dry Mitscherlich pulp was treated in a circulating digester. Enough 1 per cent sodium hydroxide solution (22 liters) was added to give a consistency of 5.9 per cent. Circulation was started, and the pulp was cooked for 3 hours at 95° C. After this treatment, a bottom drain valve was opened, and the hot liquor was allowed to drain off. The pulp was then washed 4 times with water. The drain valve was closed, another fresh charge of sodium hydroxide was added, and the process was repeated. A total of 7 such treatments were given. The pulp was then removed from the digester by hand, washed thoroughly with cold water, and treated for 5 minutes with 1 per cent acetic acid by weight at 3.5 per cent consistency. Another thorough washing with cold water was given, the pulp was pressed to about 25 per cent dry, broken up by hand, and stored in an air-tight can. In addition, a commercial West Coast bleached sulfite was given multistage treatments identical to that given the Mitscherlich above.

Alpha-cellulose was determined in the usual manner. Beater runs were made on the original and treated sulfite using Institute Method 405.

The complete beating data will be found in Table XXV. The evaluations of the two pulps at 500 cc. freeness are shown in Tables XXVI and XXVII, and the alpha cellulose content of each is given.

TABLE XXV

BEATING CHARACTERISTICS OF MULTISTAGE-TREATED PULPS

Time min.	Freeness cc.	Basis Weight 25x40-500	Caliper mils	Apparent Density	Mullen pts./#	Tear Factor	Opacity	M.I.T. Fold
Original Sulfite (Mitscherlich)								
0	835	47.6	3.1	15.3	115	1.01	66.8	835
20	590	48.4	2.9	16.8	133	0.84	53.	1780
40	290	47.0	2.8	17.0	118	0.72	45	4100
Multistage-Treated Mitscherlich								
0	845	44.5	3.2	13.9	56	2.09	76	60
20	650	44.5	2.8	15.9	108	1.03	69	1338
40	395	43.9	2.5	17.6	105	1.04	67	1390
60	235	44.4	2.4	18.5	115	0.83	60	1926
Original West Coast Sulfite								
0	865	47.2	4.8	9.8	21	1.90	75	
20	575	46.1	3.5	13.2	74	1.08	69	
40	290	45.2	3.2	14.1	82	0.84	64	
Multistage-Treated West Coast Sulfite								
0	860	50.7	5.5	9.2	16	1.83	75	
20	720	47.6	3.8	12.5	59	1.47	74.5	
40	475	47.4	3.5	13.5	68	1.12	73	
60	285	46.5	3.0	15.5	75	0.93	73	

TABLE XXVI

COMPARISON OF ORIGINAL AND MULTISTAGE-TREATED SULFITE AT 500 CC. FREENESS

	Original	Multistage
Time to develop--min.	26	33
Mullen--pts./lb.	130	109
Tear factor	0.80	1.04
M.I.T. Fold	2500	1360
Opacity	50	68
Apparent Density	17.0	17.0
Alpha-cellulose--%	80.5	91.2

TABLE XXVII

COMPARISON OF ORIGINAL AND MULTISTAGE-TREATED WEST COAST SULFITE AT 500 CC. FREENESS

	Original	Multistage
Time to 500 cc.--min.	25	38
Mullen--pts./lb.	77	68
Tear factor	1.00	1.16
Opacity	68	74
Apparent density	13.5	14.0
Alpha-cellulose--%	83.0	89.0

It is seen that the indications of the previous work have been borne out. Purification of a low alpha-cellulose sulfite pulp with hot caustic solutions yielded a purified pulp having the same alpha-cellulose content as the bleached kraft pulp purified by cold 10 per cent caustic. The changes in physical characteristics as a result of the purification process are shown in Table XXVIII.

Thus, the treatment is the important factor governing the papermaking qualities of an alpha pulp, and it has been shown that mild treatments will produce a pulp of fairly high alpha-cellulose content which still retains desirable papermaking properties and results in pulps characterized by high opacity.

L. PHOTOMICROGRAPHS OF BEATEN AND UNBEATEN STOCK

Photomicrographs were made of slides of several of the pulps. A magnification of 250 diameters was used, and light and dark field views were taken. The pictures were made with the fibrils in focus, because of which some of the fibers may appear hazy.

TABLE XXVIII

COMPARISON OF MULTISTAGE TREATMENT WITH
COLD 10 PER CENT CAUSTIC TREATMENT

Pulp	Alpha-Cellulose %	Time to 500 cc. Freeness min.	Increase %	Mullen pts./#	Retention %	M.I.T. Fold	Retention %	Tear	Increase %	Opacity	Increase %
Original Kraft	81.4	48		103		950		81		63	
10 Per Cent Treated	91.8	89	85	48	47	30	3	95	17	80	27
Original Mitscherlich	80.5	26		130		2500		80		50	
Multistage Treated	91.2	33	19	109	84	1360	54	104	30	68	36
Original West Coast Sulfite	83.0	25		77		----		100		68	
Multistage Treated	89.0	38	52	68	88	----	--	116	16	74	9

The photographs show that unbeaten mercerized pulp is considerably twisted and shrunken (Figures 17 and 22). The fact that portions of a fiber may be in focus while other portions may be far out of focus shows the twisted nature of the material.

A comparison of Figures 16 and 18 will show that beaten mercerized pulp is reduced to much finer fragments and develop fewer and shorter fibrils than normal pulps. The fact that the fibers have not been opened by the beating as much for the regenerated pulps as for the original pulps is also seen. Figure 19 shows the multistage-treated sulfite beaten to a low freeness. This treatment does not shrink the fibers, and the fibrils are longer and more plentiful than is the case with mercerized pulp. Figures 20 to 23 show somewhat the same results for rag stocks, although the differentiation between beaten unmercerized and mercerized rag stocks is not quite as apparent as with the wood pulps.

These photomicrographs demonstrate the fact that beaten mercerized pulps are of an entirely different character than are beaten normal pulps.

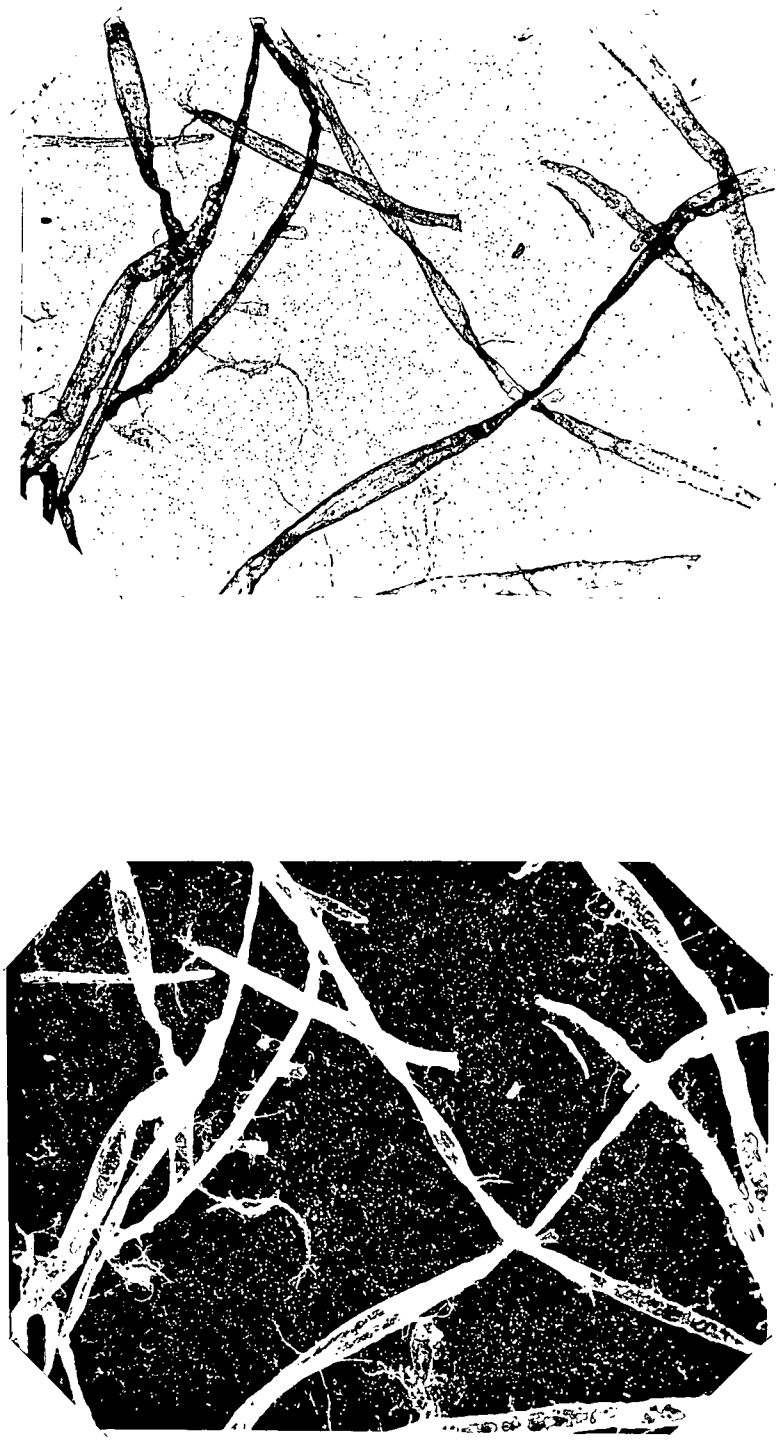
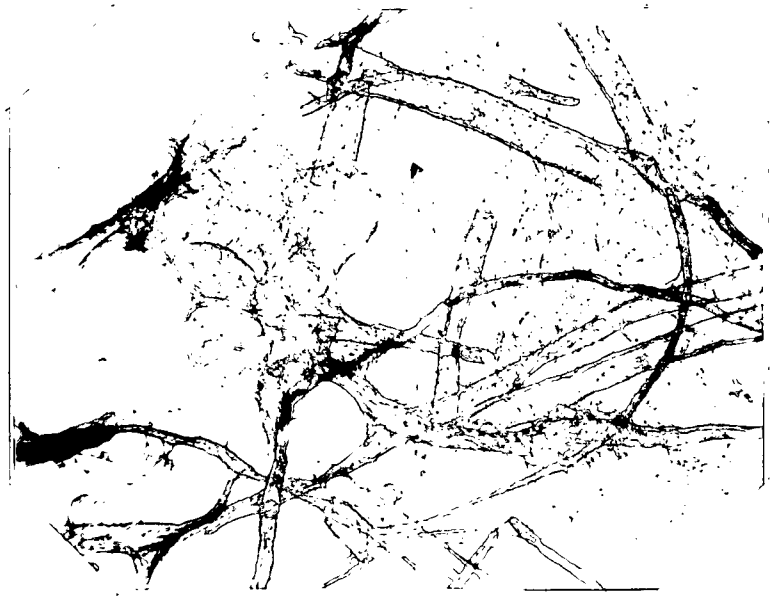


FIGURE 15

Unbeaten Original Sulfite--860 cc. Freeness



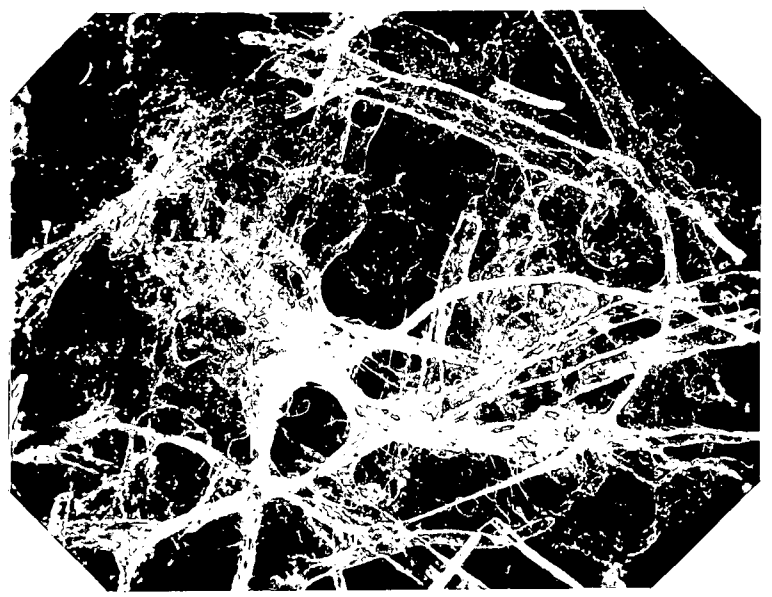
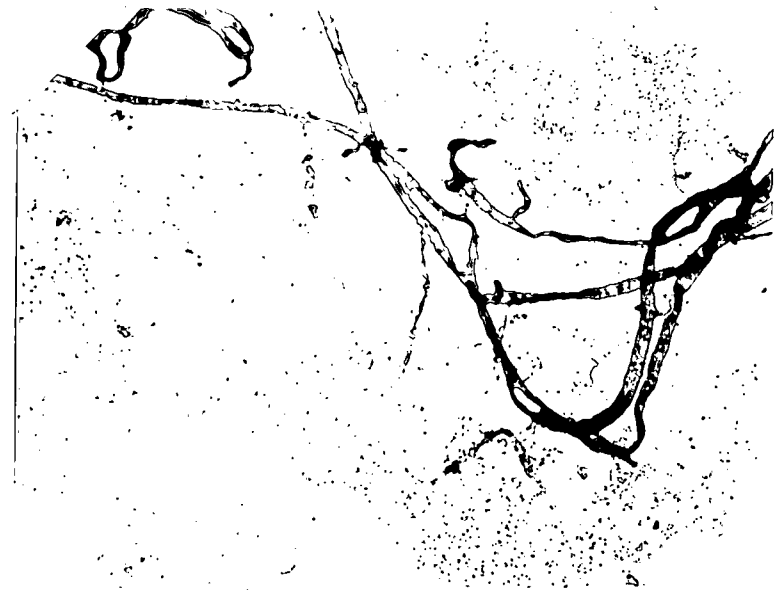


FIGURE 16

Beaten Original Sulfite--275 Freeness



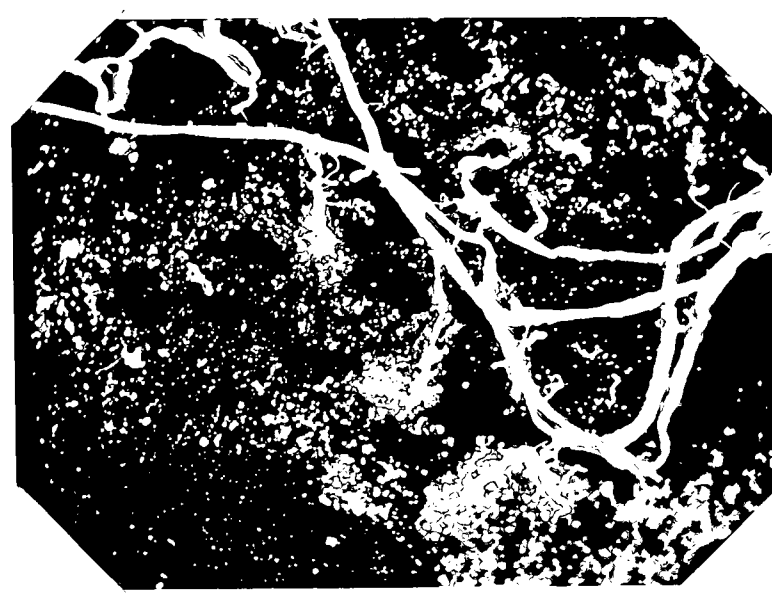


FIGURE 17

15% NaOH-Treated Sulfite--860 cc. Freeness

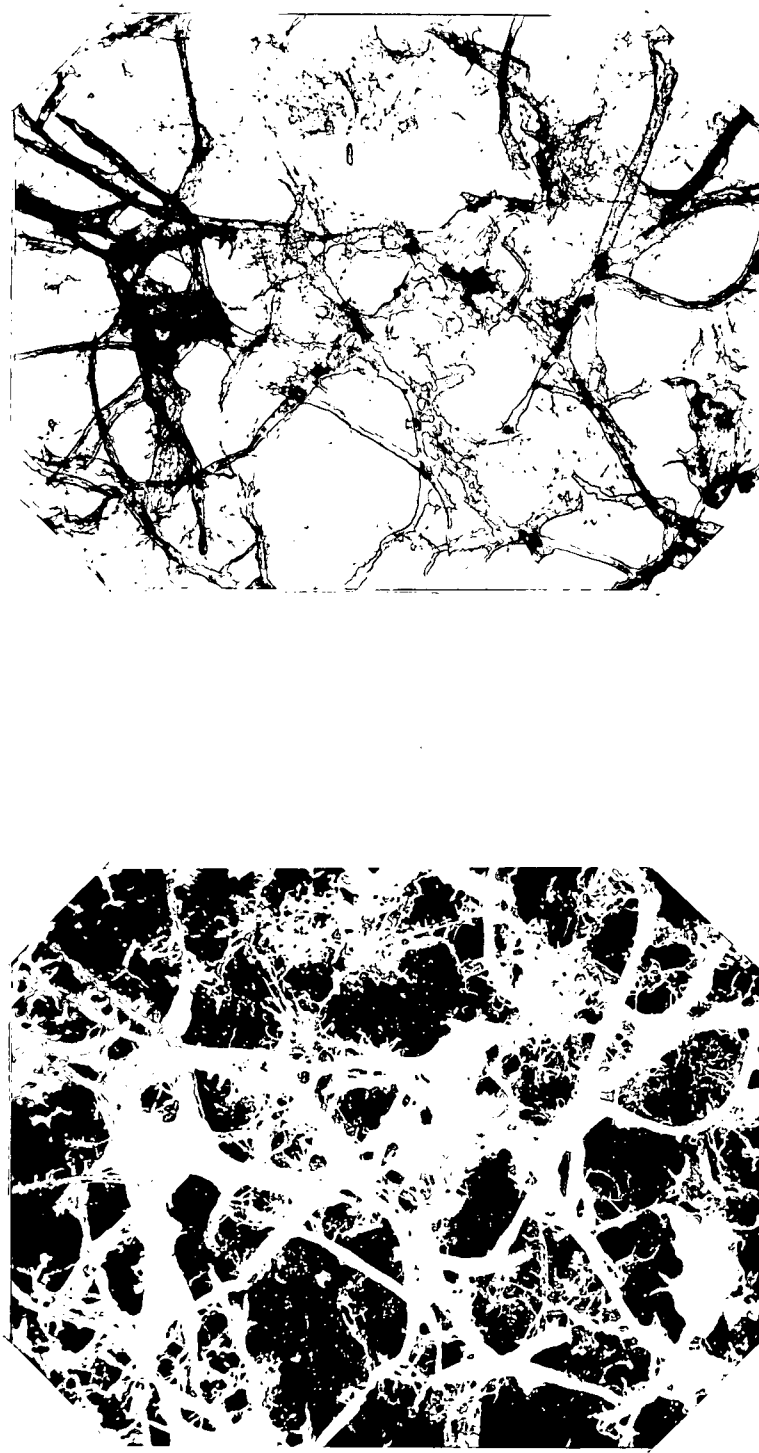
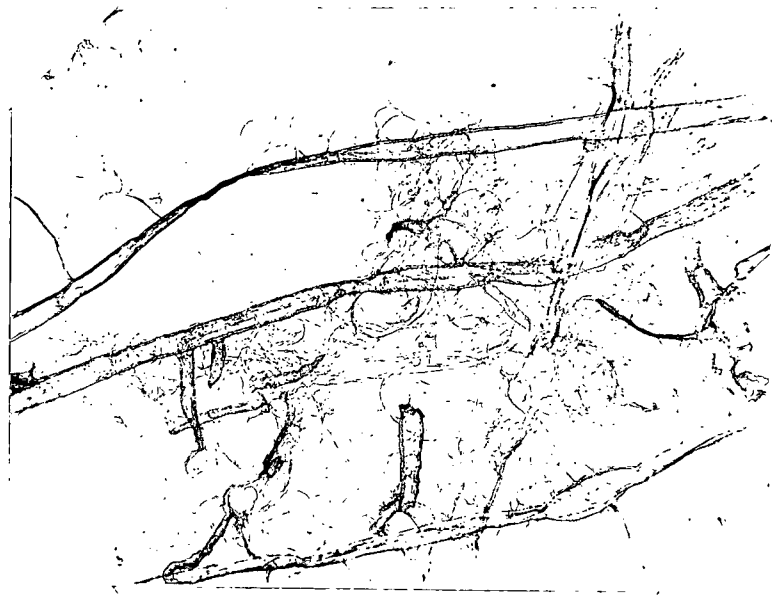


FIGURE 18

15% NaOH-Treated Sulfite--400 cc. Freeness



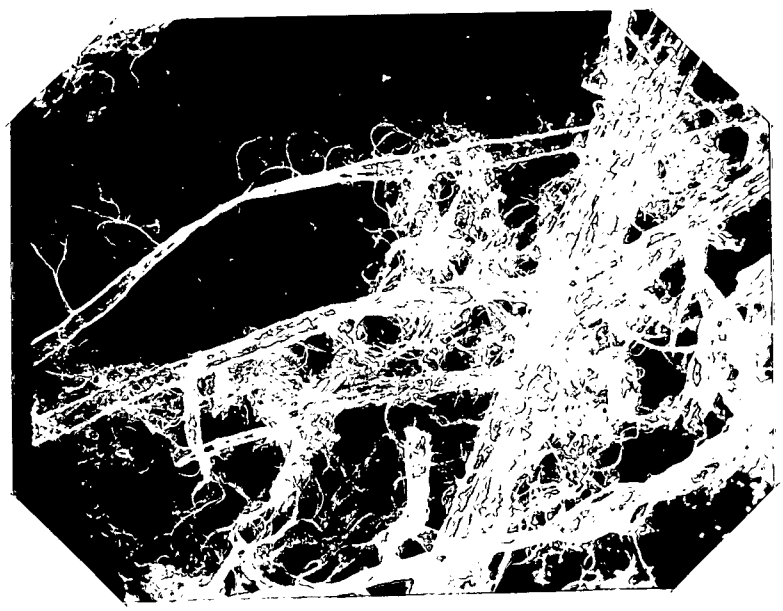


FIGURE 19

MULTISTAGE-TREATED SULFITE--250 cc. Freeness

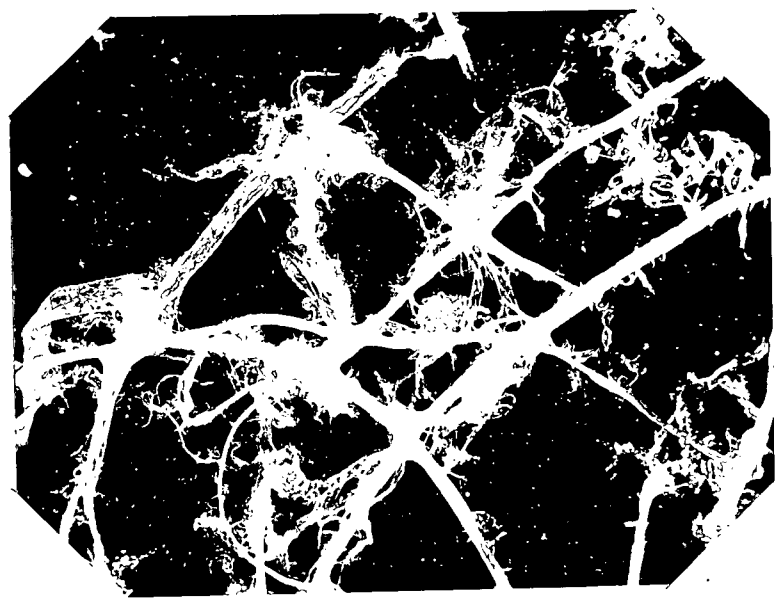


FIGURE 20

Unbeaten Rag Stock--860 cc. Freeness

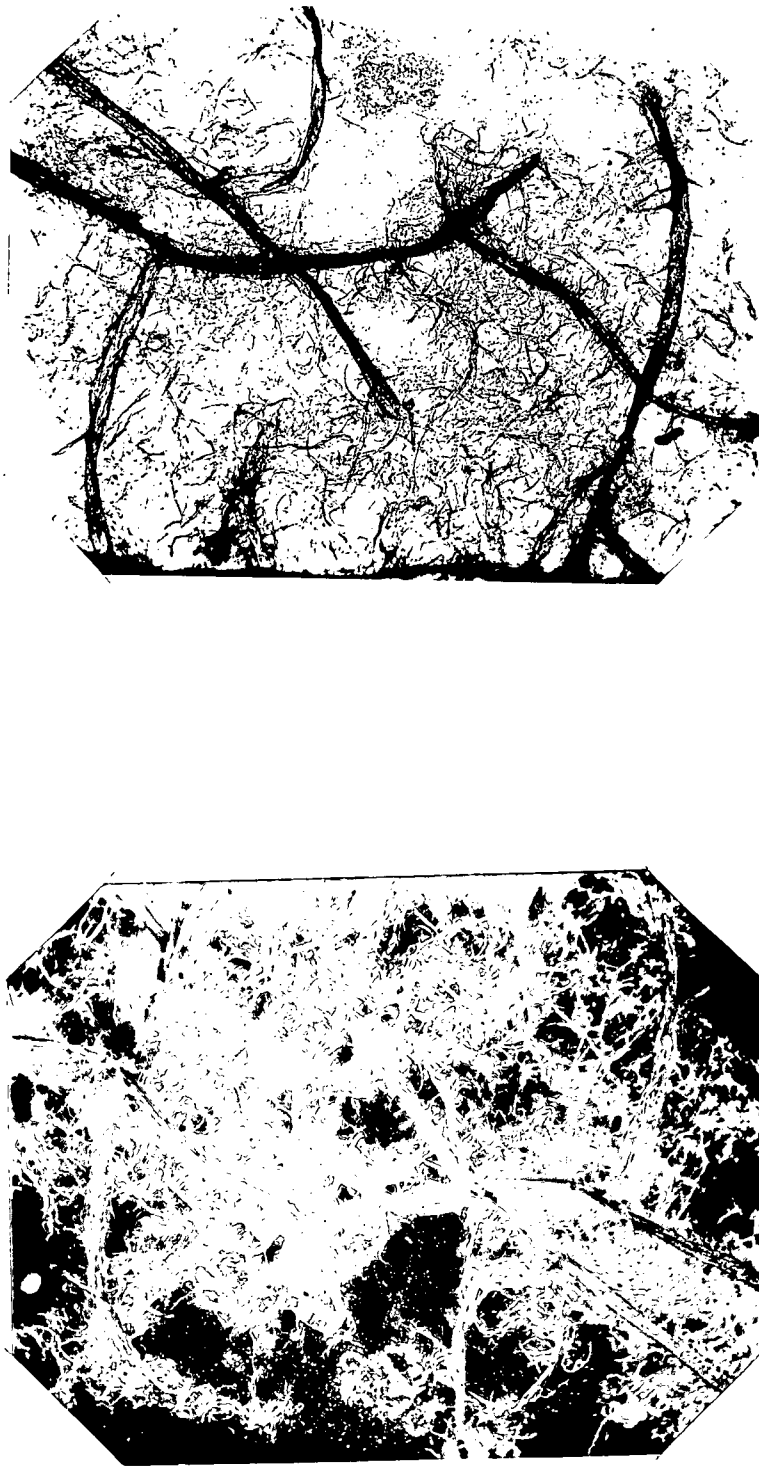


FIGURE 21

Beaten Rag Stock--300 cc. Freeness

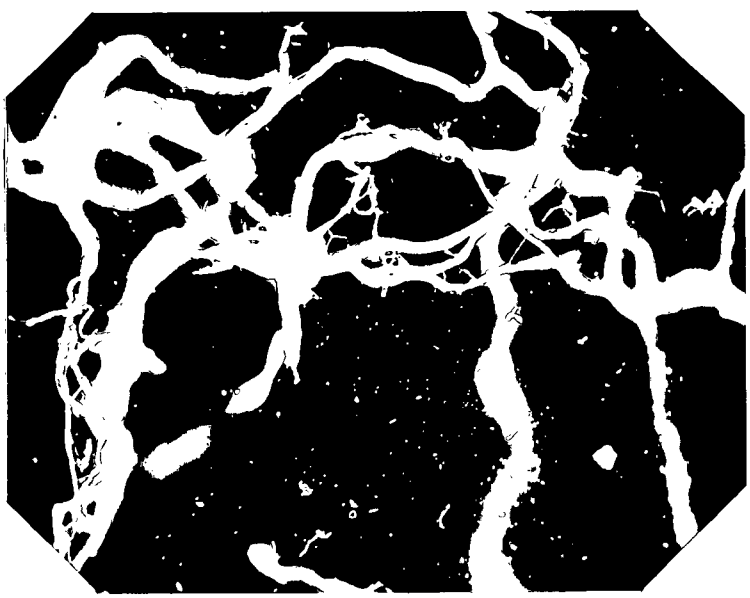


FIGURE 22

15% NaOH-Treated Rag--850 cc. Freeness

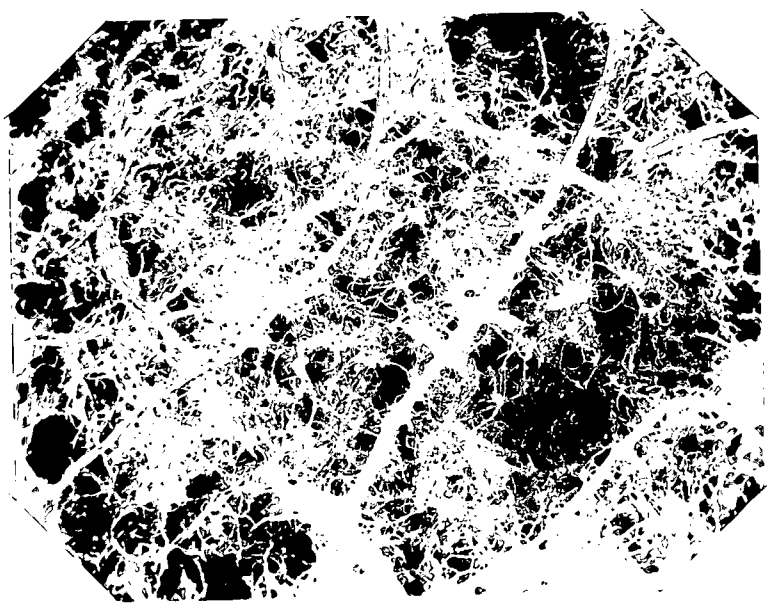


FIGURE 23

15% NaOH-Treated Rag--320 cc. Freeness

M. ATTEMPTS TO DEVELOP PAPERMAKING PROPERTIES IN MERCERIZED PULPS

A few preliminary experiments were conducted in an attempt to develop papermaking properties in mercerized pulps by simple chemical or physical means. The 15 per cent alkali-treated sulfite was used for these investigations.

The following are the simple chemical treatments used:

1. A sample of the mercerized pulp was allowed to stand in water for three weeks.
2. Another sample was boiled in water for one hour.
3. A third sample was boiled in 1 per cent acetic acid for one hour.

The equilibrium moisture of handsheets at 65 per cent relative humidity was used as a control test. From the results given in Table XXIX it is seen that the treated pulp still had the high hygroscopicity characterizing mercerized cellulose, and the sheets still had the usual high caliper. These simple chemical treatments proved ineffective in improving the sheet-making characteristics of the mercerized pulp.

TABLE XXIX

EFFECT OF SIMPLE TREATMENTS UPON THE EQUILIBRIUM MOISTURE CONTENT OF HANDSHEETS OF MERCERIZED SULFITE

	Caliper mils	% Water at 65% R.H.
Original unmercerized	3.5	9.73
Original mercerized	10.5	11.17
In water three weeks	10.5	11.93
Boiled in water	10.5	11.66
Boiled in acetic acid	10.5	11.44

Since Mullen and fold strength are associated with increased sheet density, the effect of pressure was next investigated. Sheets were made as usual from the 15 per cent alkali-treated sulfite. Different pressures were used in preparing the handsheets, which were then seasoned at 65 per cent relative humidity and 70° F. for 6 hours, after which time physical tests were made. The results presented in Table XXX show that a pressure of 750 pounds per square inch is required to reduce the caliper to 0.0042 inch. This thickness is still quite high. Previous data have shown that the unbeaten hot 1/2 per cent alkali-treated sulfite has a caliper of 4.0 mils and little strength. Thus, the pressures used were not sufficient to reduce the caliper to an extent where enough fiber-to-fiber bonds are formed so that good strength is developed. Higher pressures would not be practical for sheets of such low original strength, due to difficulties in handling. That the pressures used were considerable may be seen from the fact that a pressure of 750 pounds per square inch means a total force of 11.6 tons for the regular standard sheets (200 square cm. area).

TABLE XXX

EFFECT OF PRESSURES ON STRENGTH OF HANDSHEETS OF REGENERATED SULFITE

Pressures #/sq. in.	Basis Weight 25x40-500	Caliper mils	Apparent Density	Mullen pts./lb.	Opacity	M.I.T. Fold
50	48	9.5	5.1	12.5	70	0
100	50	8.5	5.9	12	70	0
250	52	6.5	8.0	11.5	70	0
500	50	4.8	10.5	11.9	69.5	0
750	49.4	4.2	11.8	12.2	69.5	0

From handling the sheets, indications were that if the caliper were reduced still more, some strength would be realized. The sheets of 4.2 mils caliper were definitely stronger than those of 9.5 caliper, even though the strength was still too low to be detected by the usual testing methods; however, to reduce the caliper to such a degree that good strength is obtained would require enormous pressures.

V

CONCLUSIONS

From the data obtained, the following conclusions may be drawn:

1. Wood pulps purified by alkaline treatments show relatively small loss of papermaking qualities unless sodium hydroxide of such strength is used that the cellulose has been mercerized in the process; for this case, where a concentration of sodium hydroxide of 10 per cent or greater is used, pronounced losses in papermaking properties are shown. That this loss cannot be due simply to the removal of the hemicelluloses is proved by the fact that rag stocks, subjected to mercerizing treatments, give practically the same results as wood pulps and yet are changed very little chemically. Thus, it is the treatment which is the important factor in determining the papermaking properties of purified pulps, not the materials removed.

2. Mercerized fibers require higher concentration of cuprammonium hydroxide to produce swelling and solution than do unmercerized fibers.

3. Mercerized fibers swollen in 17.5 per cent sodium hydroxide exhibit a high pick-up of caustic and relatively small swelling. Unmercerized fibers, in contrast, swell more and pick up less caustic. Thus, the mercerization treatment yields a fiber with vastly different swelling behavior than that of unmercerized fibers.

4. The pulps of good papermaking quality (unmercerized) decrease in opacity with beating regardless of the chemical constants of the pulp, while the pulps of poor papermaking quality (mercerized) increase in opacity with beating. Such a radical change in beating behavior shows that the mercerized pulps have undergone a fundamental change as the result of mercerization and supports the belief that this treatment is responsible for the loss in papermaking properties of the mercerized pulps.

5. The effective capillary diameter of sheets from the pulps of poor papermaking characteristics is 20 times that of the pulps making satisfactory paper. This effect results from the mercerizing treatment and has no relation to the chemical composition of the various pulps. This gives further support to the hypothesis that wood pulps of high alpha-cellulose content are spoiled for papermaking by the process used in purifying them when this process involves mercerization.

6. Photomicrographs show that mercerized pulps seem to develop fewer and shorter fibrillae with beating than do unmercerized pulps.

7. Pulps of high alpha-cellulose content and good papermaking properties may be prepared by successive mild treatments. Pulps prepared this way and by the cold mercerizing process, but having much the same chemical constants, show vastly different papermaking qualities. The results are decidedly in favor of the multistage hot dilute caustic treatment.

8. The correlation between physical properties and the chemical

properties of alkali-purified pulps is not very good. This would be expected from the fact that the type of treatment has been shown to produce great changes in the papermaking qualities without appreciable chemical changes. The principal correlation is found between the alpha-cellulose content of the pulps and the opacity, on one hand, and the apparent density on the other. The data are insufficient, however, to permit an unqualified conclusion.

9. It is shown that the absorption of light by sheets is increased by beating and by calendering.

VI

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