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Doctor's Dissertation

The Role of the Hydroxyl Groups of Cellulose and Pentosans in the Water-binding Phenomenon in the Beating Process

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May, 1942

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THE ROLE OF THE HYDROXYL GROUPS OF CELLULOSE AND PENTOSANS IN THE WATER-BINDING PHENOMENON IN THE BEATING PROCESS

A thesis submitted by

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INTRODUCTION

The affinity of cellulose for water has commonly been attributed to its hydroxyl groups. Hygroscopic studies (1, 2) on pulps acetylated to various degrees have shown that, as the hydroxyl groups are covered by acetyl groups, the affinity of the cellulose for water is progressively decreased.

The bonding of paper has also been attributed to the hydroxyl groups of cellulose and is thought to occur through secondary valences arising from them. Two recent investigations by independent workers have shown that, as the hydroxyl groups of cellulose are covered up by acetyl groups, the strength properties of the paper prepared from the cellulose are steadily reduced. Brown and Harrison (3) found that the strength properties of kraft pulp decreased considerably with increased acetyl content. Working with fibrous cellulose acetate prepared from rag stock by a very mild method of acetylation, Bletzinger (4) found an initial increase in strength properties to a maximum at 6.1 per cent acetyl content, and then a rapid decrease with the introduction of more acetyl groups.

If both the bonding characteristics of paper and the hygroscopic characteristics of cellulose depend upon the hydroxyl groups of cellulose, there should be a correlation between the two. Methods are available for measuring both the water taken up by cellulose from air at various vapor pressures and that taken up from suspension in liquid water. In this investigation these methods have been applied to samples of cellulose acetate prepared from rag stock and from

Mitscherlich pulp, and the results are compared with the strength characteristics of sheets prepared from the acetates. If both the water-binding properties of cellulose and the bonding strength of paper are dependent on the hydroxyl groups of cellulose, this study should show a correlation between the two, and it should also explain the initial increase in strength with low degrees of acetylation as found by Eletzinger.

Several investigators have noted that pentosans, either originally present in the pulp or added to the pulp, increase the strength of the sheet made from the pulp. If the bonding strength of a sheet arises through the hydroxyl groups of the cellulose, it is logical to assume that, if shorter chains of the pentosans are interwoven with the longer cellulose chains, the forces between the hydroxyl groups of the cellulose and those of the pentosan should lead to an additional bonding force, but acetylated pentosan--that is, pentosans whose hydroxyl groups have been covered by acetylation--should be without effect. The effect of pentosans on the bonding strength of a sheet was studied by beating rag stock alone, rag stock to which pentosans had been added, rag stock to which acetylated pentosans had been added, and acetylated rag stock to which pentosans had been added. In the study of the action of the pentosans two factors had to be considered. (1) By adding pentosans, more hydroxyl groups are introduced into the pulp and, thus, the opportunity of water-binding is increased. As the water is removed the bonding is accomplished either (a) between hydroxyl groups of the pentosan chain or (b) between those of the pentosans and of the cellulose chains. (2) The pentosans act merely as a cementing material or glue.

HISTORICAL REVIEW

For convenience and clearness, the historical review is divided into three parts. (1) The effect of hydroxyl groups on the bonding strength of paper, (2) the effect of hydroxyl groups on the water-binding characteristics of cellulose, and (3) the effect of pentosans on the bonding strength of paper.

EFFECT OF HYDROXYL GROUPS ON THE BONDING STRENGTH OF PAPER

Urquhart (5) believed that, when cellulose is formed in the plant, it is laid down in the presence of water and that the hydroxyl groups probably have water molecules attached. As the fiber dries, these hydroxyl groups liberate the water and tend to rearrange so that their residual valences will be mutually satisfied by adjacent molecules which results in the bonding together of the cellulose fibers. When the cellulose is again placed in water, some of the molecules reattach themselves to water to give a looser form, but the fiber structure is still retained.

The bonding forces that hold the fibers together in a sheet of paper were considered by Cottrall (6) to depend upon the number of fiber-to-fiber contacts to form the bonds through the linkage of free hydroxyl groups of the cellulose. These contacts can be produced through wet pressing, fibrillation in a beater, or friction in a Lampén mill.

Doughty (7) divides the beating process into two stages. In the first stage an absorption of water is the preponderant effect with an increase in tensile strength at constant solid fraction. In

the second stage, the decrease in fiber size is most important, and the strength increase is proportional to the solid fraction. The effect of the second stage can be duplicated by pressing, but the first cannot.

The views of Campbell (8, 9) were very similar to those of Cottrall and Urquhart and seem to represent the most plausible explanation yet advanced for the bonding strength of paper. Campbell considered that the purpose of the beating operation is to increase the surface by fibrillation and to reduce the mean fiber size, thereby reducing the rigidity of the fibers. When the sheet dries, the surface tension of the water between the fibrous elements, which may be in the order of several hundred atmospheres, draws the flexible fibers into intimate contact and "as various elements of the structure are brought close enough to each other, additional forces of attraction come into play--the forces of the molecular attraction of the cellulose for cellulose, identical in kind with those holding molecules in the crystal." These forces bind the fibers together and give rise to the strength of the sheet.

The theory of Campbell is in point well supported by the work of Kress and Bialkowsky (10), which showed that the beating medium must wet and swell the fiber if strength is to be developed upon beating. When ethylene glycol, methyl alcohol, formamide, and other liquids that swell cellulose were used as the beating medium, the pulp developed strength properties similar to those obtained when water was the beating medium; however, when pulp was beaten in fuel oil, butyl alcohol, and other liquids that do not swell the fibers,

only a cutting action was obtained with no development of strength.

Bletzinger (4) found that fibrous cellulose acetate of 25 per cent acetyl content was hardly wet by water, and that practically no strength was developed when it was beaten in water. This same acetate, however, was very well wet by acetone and, when it was beaten in acetone, it gave strength results even greater than those obtained by beating unacetylated stock in water.

The beating action, then, must be carried out in a medium that thoroughly wets or swells the fibers. As the sheet dries, the surface tension of the liquid draws the fibers into intimate contact, so that the secondary valences (or hydrogen bonds) may come into play. That the bonding forces actually arise from the hydroxyl groups of the cellulose is seen from Bletzinger's work and appears to be confirmed by the work of Brown and Harrison (3).

Bletzinger studied the effect of hydroxyl groups on the bonding strength of paper by covering part of the hydroxyl groups with acetyl groups, using a method which practically did not chemically degrade the cellulose. With increasing but limited acetyl content, there was an increase in bursting strength of the beaten pulp, a maximum being observed at an acetyl content of 6.1 per cent. With further increase in acetyl content (up to 25 per cent) a rapid decrease in bursting strength occurred, 25 per cent being the maximum amount that could be introduced in ninety days by the mild method of acetylation used. The freeness passed through a minimum at 6.1 per cent acetyl content, whereas tearing and tensile strengths and

apparent density steadily decreased with increasing acetyl content without showing either maximum or minimum. Eletsinger offered two possible explanations for this behavior.

(1) The effect of partial acetylation may consist of an opening up of the internal structure of the fiber, resulting in the exposure of more hydroxyl groups to hydration with subsequent increased bonding than are available in the unacetylated fiber. Further acetylation, however, would cover these newly exposed hydroxyl groups and, therefore, reduce the bonding force.

(2) After finding that the mercerization of rag stock with sodium hydroxide caused a loss in strength of the paper sheet prepared therefrom, which was in proportion to the extent of the mercerization, Probst (11) postulated that the loss in strength might be at least partly due to the accessibility of an excessive number of hydroxyl groups, causing a stable film of water to surround the micelles and single chain molecules and thus preventing bonding in the usual manner. The introduction of a small amount of acetyl groups into the rag stock might reduce this film, but sufficient uncovered hydroxyl groups would still be present to bond strongly the fibers together upon beating. However, this explanation is rather improbable because the rag stock which Eletsinger used was not mercerized, and thus did not possess the increased accessibility of hydroxyl groups upon which Probst based his hypothesis.

Brown and Harrison (3), studying the effect of acetylation on the beating of kraft pulp, also found the strength properties to

decrease rapidly with acetyl content. A sample of lap, cylinder-dried kraft pulp and two samples of lap, vacuum-dried kraft pulp were acetylated under different conditions. In all three cases beater runs on the materials gave sheets that had decreasing bursting, tearing, and tensile strengths with increasing acetyl contents. In the case of the cylinder-dried pulp there was little change in freeness development until a combined acetic acid content of 37.5 per cent had been reached. The freeness values of the materials prepared from vacuum-dried pulps were irregular until about 30 per cent combined acetic acid had been introduced. Above this point, the pulps were very free at all beating intervals. It may be mentioned here that Brown and Harrison did not observe the phenomenon of increase in strength within the range of very low acetyl contents--i.e., from zero up to about 6 per cent acetyl content. Even with as low an acetyl content as 3.94 per cent (= 5.5 per cent combined acetic acid), the physical strength properties of their acetylated kraft pulp were considerably lower than those of the unacetylated fiber.

EFFECT OF HYDROXYL GROUPS ON THE WATER-BINDING PROPERTIES OF CELLULOSE

The effect of acetylation and other types of esterification upon the water-binding capacity of cellulosic materials has long been known. Particularly, Sheppard and Newsome (2) made extensive investigations of the water absorbed by cellulosic materials and cellulose acetates at various vapor pressures. Cellulose acetates and cellulose regenerated from cuprammonia solution, viscose, and esters of cellulose, as well as mercerized cellulose, were shown to give hysteresis loops on humidification and dehumidification similar to

those obtained with cellulose. The sorption of mercerized cellulose and regenerated celluloses was fairly constant and higher than that for natural cellulose.

Harris and Purves (12), by forming a thallium compound with exposed hydroxyl groups, methylating, and measuring the change in methoxyl content, found mercerization to increase the "effective internal surface" of ramie fiber, drastic mercerization however to reduce this surface below that of the untreated fiber.

If each hydroxyl group in cellulose held one water molecule, cellulose could take up some 33 per cent of water, but Sheppard and Newsome (2) have pointed out that even cellulose hydrate—that is, regenerated cellulose—takes up only about 23 per cent of water and native cellulose about 16 per cent water at 25° C. X-ray examination has shown that the unit cell of regenerated cellulose exhibits dilation in the two directions at right angles to its length. X-ray analysis has shown also that adsorption of water is intermicellar rather than intramicellar, and that the primary process appears to be the attachment of water molecules to hydroxyl groups exposed on the micelle surfaces in the intermicellar spaces. Anything that will open up the intermicellar space so that more hydroxyl groups are exposed should give an increase in the amount of water absorbed. On the other hand, if some of the hydroxyl groups are covered, the water-binding properties should decrease.

Sheppard and Newsome have pointed out that the shape of absorption curves obtained at different humidities, as well as heat

of absorption studies, shows that much of the water absorbed by the fiber at higher humidities is much more loosely bound than the first water that is absorbed. It appears that about five per cent of the water is held by primary sorption to hydroxyl groups in cellulose and about seven per cent by regenerated cellulose, but the total amount held by cellulose is about 16 per cent. If cellulose is acetylated, the water absorbed decreases with increasing degree of acetylation, and cellulose triacetate holds only about nine per cent of water. That so much water is held by a fiber with all of its hydroxyl groups rendered inactive is explained by the assumption that this water goes into the microscopic and ultramicroscopic capillaries of the material, because completely acetylated sugars—e.g., glucose pentaacetate and cellobiose octaacetate, representing single molecules in contrast to the aggregate of molecules in the cellulose fiber—absorb only about two per cent of water.

Filby and Mease (13), after a study of the volume relations of the cellulose-water system, concluded that only about four per cent of the water is absorbed by the cellulose itself and that the remainder is held in the capillaries. They also found that the absorption of different alcohols on cellulose (expressed in moles per gram of cellulosic material) decreases rapidly with increasing number of carbon atoms in the alcohol and becomes approximately constant with butyl alcohol. Sheppard and Newsome (14) suggested that the larger groups appear to fill the intermicellar spaces so that more alcohol cannot enter.

The effect of etherfication upon the water-binding capacity is similar, and yet again different from esterification. Methylcellulose, prepared with the retention of the original fibrous structure in the usual manner, is soluble in water when 1.2 to 1.6 hydroxyl groups per glucose residue are covered with methoxyl groups--corresponding to 20.8 to 26.9 per cent methyl content. If the cellulose is first dissolved in a quaternary ammonium base, it becomes soluble when only 0.6 to 0.7 groups are covered--corresponding to a methoxyl content of 10.9 to 12.6 per cent. Bock (15) has explained this difference on the assumption that methylation of cellulose in solution results in a more uniform distribution of the methoxyl groups. According to Bock, the cellulose ethers are soluble in water because the individual chains of cellulose are held apart by the ether groups so that more of the uncovered hydroxyl groups are available for hydration.

Froundjian and Jayme (16) prepared a fibrous methylated cellulose with eight to ten per cent methoxyl content--that is, below the water-solubility range--by treating unbleached pulp with dimethyl sulfate in the presence of sodium hydroxide and dioxane. After beating, the pulp showed strength properties very much greater than the unmethylated pulp. The folding strength was increased by 350 per cent, tensile strength by 100 per cent, and bursting strength by 50 per cent. In searching for the cause of this increase in strength, they investigated several methods for measuring the amount of water absorbed from liquid water itself. Finally, a method, which had previously been suggested by Ebert, was perfected to give very satisfactory results. Using this method, Froundjian and Jayme found their unmethylated pulp

bound 10.23 per cent water and their methylated product 15.9 per cent. This difference indicates that the methylation had greatly opened up the structure of the cellulose.

Possibly this is a phenomenon similar to that observed on limited acetylation. The introduction of a limited amount of either acetyl or methyl groups obviously increases the accessibility of uncovered hydroxyl groups and thus the opportunity for hydration and for subsequent bonding when the water is removed. The result is a sheet of paper having increased strength properties. The difference in behavior of the two materials, however, is seen when the degree of substitution is increased above the optimum. Further methylation results first in water solubility and then in the display of pronounced hydrophobic properties, whereas with acetylation above the optimum, the hydrophobic state is reached immediately. On the other hand, the possibility that on acetylation a state of intermediate water solubility occurs is not to be excluded. Water-soluble cellulose acetate has been described in the patent literature (17). However, in view of the severe method applied for acetylation, it would appear that in this case greater accessibility of hydroxyl groups and subsequent water solubility is a result of degradation of the cellulose rather than a loosening up of an undamaged micellar structure.

EFFECT OF PENTOSANS ON THE BONDING STRENGTH OF PAPER

Several investigators have noted that there is a relationship between the pentosan content of a pulp and its papermaking properties. Young and Rowland (18) found an approximate linear

relationship between the pentosan contents of a group of softwood pulps and their swelling in water.

Jonas and Rieth (19) beat two pulps that had practically the same copper numbers, viscosities, and lignin contents, but which had different pentosan contents. They found that upon beating, the pulp with the higher pentosan content developed the greater strength properties. They then added xylan and mannan and a mixture of the two to pulp in the beater, and found these added hemicelluloses also produced an increase in the strength of the pulp. Mannan caused a greater strength increase than did xylan.

Obermanns (20) found that, if hemicelluloses were introduced into a pulp by degrading it by drastic bleaching conditions, the rate of strength development of the pulp in the beater was increased; however, the final strength of the sheet was inferior to that of the undegraded pulp. Again, when xylan and beta-cellulose were added to rag stock, the rate of strength development was greatly accelerated and the strength of the rag stock was appreciably increased.

Heuts and Kurth (21) studied the effect of the hemicelluloses originally present in wood upon the strength and the rate of beating on pulp prepared from the wood. For this purpose, they prepared holocellulose, which is known to contain all of the noncellulosic carbohydrates of the extracted wood, i.e., without the lignin. This material developed at a very rapid rate in the beater and produced sheets of very good strength properties. A portion of the holocellulose was then extracted with 0.5 per cent ammonium oxalate at 90° C. to remove a small amount of pentosans and polyuronides. The

material thus prepared had a slightly slower rate of development in the beater and slightly lower strength properties than did the original holocellulose. Over-chlorination during preparation of a third sample produced a material with about half the original pentosan content of the holocellulose, but with a much higher beta-cellulose content. Upon beating, this material developed even more rapidly than did the holocellulose, but the strength properties were inferior due to degradation by over-chlorination.

Another sample of holocellulose was extracted with 17.5 per cent sodium hydroxide solution to obtain alpha-cellulose. This material was very slow to develop in the beater, and the strength properties were inferior to those of the other three samples.

All of these investigations clearly indicate that pentosans and short-chain cellulosic materials have a pronounced effect not only on the rate of strength development of pulp in the beater but also upon the strength properties of the finished sheet. This effect is secured in both directions with pentosans and hexosans (such as xylan and mannan) but is confined to an acceleration of the rate of strength development with degraded cellulose.

Obermanns (20) has explained the increase in strength upon the addition of hemicelluloses by the formation of a cementing layer between fibers. He also mentioned the possibility of an "affinity" between the hemicellulose and the cellulose. In view of the effect of hydroxyl groups upon the bonding strength of cellulose, the second explanation seems more plausible.

The present investigation covers the following items:

(1) Gradual acetylation of rag fibers within the lower and the higher range of acetyl contents with an attempt

(a) to confirm Bletzinger's results on the relation between degree of substitution and physical strength properties of sheets prepared from the acetylated fibers, and

(b) to establish a relation between the acetyl content and the strength properties on the one hand and the hygroscopical properties of the acetylated fibers on the other.

(2) Acetylation of wood pulp with the object of ascertaining the existence of relationships as pointed out in (a) and (b).

(3) Preparation of sheets from beaten (or disintegrated) acetylated fiber with acetone as the medium to attempt to confirm Bletzinger's results on rag stock and to establish corresponding data on acetylated wood pulp.

(4) The addition of unacetylated and acetylated pentosans (in the form of xylan) to rag stock and to wood pulp in an attempt to elucidate the strength increasing effect of pentosans in papermaking materials.

EXPERIMENTAL PROCEDURE FOR ACETYLATION AND BEATING

RAW MATERIAL

Bletzinger chose rag stock as the most suitable material for his investigation because of its high degree of polymerization and its low content of noncellulosic material. The same type of material was used in this investigation. A local rag paper mill

supplied fifty pounds of their No. 1 hard rag stock, which had been prepared from new unbleached muslin. It had been left in the drainers for only about two days, and no degradation, possibly due to bacterial action, should have taken place.

In addition, a bleached Mitscherlich sprucewood pulp was used to determine whether acetylated wood pulps behave in a way similar to acetylated rag stocks in beating and possess the same water-binding characteristics.

The rag stock and Mitscherlich pulp were analyzed for TAPPI viscosity, pentosan content, copper number, and alpha-cellulose content by Institute Methods; for (original) acetyl content by the method described on page 23 of this thesis; and for Staudinger viscosity according to the method described by Heuser and Green (22). The results of these analyses are given in Table I.

TABLE I

CHEMICAL ANALYSES OF RAG STOCK AND MITSCHERLICH PULP

	Rag Stock	Mitscherlich Pulp
Molecular weight (Staudinger)	233,400	166,400
Degree of polymerization (Staudinger)	1,441	1,027
TAPPI viscosity	96.0	61.7
Alpha-cellulose, %	98.15	85.06
Copper number	0.42	2.06
Pentosan content, %	0.0	5.7
Original acetyl content, %	0.0	0.26

PREPARATION OF RAG STOCK

Bletzinger (4) found that rag stock could be reduced to a physical state suitable for being processed in laboratory testing equipment by cutting it in a laboratory beater for a short time at a very low consistency. This cut rag stock had a fiber length and a fiber distribution of such nature that good formation could be obtained upon processing in laboratory testing equipment, and the strength properties of the sheets formed from the beaten stock are sufficient to show changes that occur upon covering up the hydroxyl groups with acetyl groups.

To determine the best conditions for cutting the rag stock, used in the present investigation, a sample of the material was cut in a 5-pound Valley beater at 0.3 per cent consistency for ten minutes with 25 pounds on the bedplate. Samples for freeness determination were taken at one-minute intervals after the first six minutes. The results of the freeness tests were as follows:

Beating Time min.	S. R. Freeness cc.
6	760
7	730
8	700
9	675
10	645

Another sample of the rag stock was cut under the conditions given above for seven minutes. Portions of the cut material were then beaten in the Lampén mill at 0, 30, 60, and 90-minute intervals. Sheets were made at each interval and tested for basis weight, caliper,

bursting strength, and tearing strength. The results, which are given in Table II, show that the strength development characteristics of the treated material are satisfactory for this investigation.

TABLE II

STRENGTH PROPERTIES ON TRIAL BEATER RUN ON CUT RAG STOCK

Beating time, min.	0	30	60	90
Freeness, cc.	640	600	530	410
Basis weight (25x40--500)	40.5	38.9	40.7	47.8
Caliper	4.2	3.8	3.7	4.1
Apparent density	9.7	10.2	11.0	11.7
Bursting strength, lb./sq.in.	28.6	28.5	27.5	27.7
(Burst/basis weight)100	70.5	73.4	67.5	53.0
Tearing strength	164	143	132	125
Tear/basis weight	4.05	3.72	3.24	2.61

To determine if the cut rag stock could be acetylated under the conditions to be used, one sample of the material was acetylated for one hour and another sample for twelve hours. Acetyl determinations showed the former to have an acetyl content of 7.7 per cent and the latter one of 10.3 per cent; therefore, this material appears to acetylate normally.

From these experiments it was concluded that the rag stock cut for seven minutes had suitable characteristics both from the standpoint of strength development on beating in the Lampén and of acetylating characteristics.

To provide a supply of raw material for the main investigation, 25 pounds of the rag stock were cut at 0.3 per cent consistency for seven to eight minutes in the 5-pound Valley beater with 25 pounds on the bedplate. The cut material was thickened by draining on a cloth and transferred to an experimental blow pit where all of the material from the 38 runs in the 5-pound beater were thoroughly mixed by stirring for one hour with a Unipower Agitator. The mixed material was then pressed to about "25 per cent dry" in a wine press, torn by hand into small pieces, and spread out to air-dry. The dried material was sampled for moisture determinations and then stored in sealed glass jars. Another 25 pounds of the rag stock were not cut in the beater but were only torn into large pieces, air dried, and stored for possible future use.

PREPARATION OF MITSCHERLICH PULP

Twenty-five pounds of the Mitscherlich pulp in wet lap form were thoroughly mixed for one hour in the experimental blow pit, pressed in the wine press, torn up into small pieces and spread out to air dry. The dried material was sampled for moisture tests and stored in sealed glass jars.

METHOD OF ACETYLATION

The method of acetylation used in this investigation had to be one that did not degrade the cellulose fibers. Bletzinger found that the method of Hess and Ljubitsch (23) met these requirements. However, in order to avoid any effect of mercerization and possible oxidation, Bletzinger omitted the steeping of the cellulose

in strong alkali before introducing it into the acetylation mixture of pyridine and acetic anhydride--a step provided in the original method. Bletzinger's results showed that this modified method of acetylation did not reduce the tensile strength of the individual fiber and did not change the degree of polymerization of the cellulose. Moreover, pulp regenerated from the acetylated fiber prepared by this method had the same characteristics as the original cellulose.

The method of acetylation used in the present investigation for obtaining acetylated cellulose from rag stock with acetyl contents above ten per cent was as follows: Rag stock equivalent to 65 grams of oven-dry material was placed in a half-gallon, glass-topped jar, covered with pyridine and allowed to soak overnight to remove moisture from the pulp and to wet the fibers with pyridine. Then it was defibered by means of a Lightnin mixer for five minutes, and the pyridine was removed with suction on a Büchner funnel. About 200 cc. of the pyridine remained in the pad. The pulp pad was then returned to the jar, the Lightnin mixer started, the pyridine-acetic anhydride mixture added, and the mixture stirred for five minutes.

The acetylation mixture was prepared by the addition of fresh acetic anhydride to the acetylation mixture filtered from previous acetylations. The total acetylation mixture, including the pyridine remaining in the pulp pad, amounted to 10 cc. of acetic anhydride and 16 cc. of pyridine per gram of oven-dry pulp, or a volume of 1690 cc. containing 38.4 per cent acetic anhydride by volume.

The jar containing the acetylation mixture was placed on a rotating stirrer for 24 hours and then in a water bath at 40° C. for several days. At the end of the acetylation time, the acetylation mixture was removed with suction and the filtrate saved for future acetylations. The pulp pad was transferred to a one-liter beaker and washed three times with pyridine to remove the red color formed during the acetylation. The pyridine was removed by three washings with alcohol, and the alcohol removed by three washings with ether. Air was then sucked through the pad for several minutes to remove the ether, and the material was finally torn into fine shreds and allowed to air dry for several hours before it was stored in sealed glass jars.

The acetyl content was controlled by the time that the material was left in the bath at 40° C. By this method a few per cent of acetyl is introduced into the pulp in a few minutes, after which the rate is considerably retarded.

As this study was concerned primarily with materials of low acetyl content, the acetylation procedure was modified to prepare such compounds. It was found that by reducing the concentration of acetic anhydride in the acetylation mixture, the initial rate of reaction could be considerably reduced.

The method for preparing pulps of very low acetyl contents was as follows: The pulp was soaked in pyridine, disintegrated, filtered, and stirred in the acetylation mixture as described above. The acetylation mixture was prepared by adjusting the mixture from previous acetylations to the desired acetic anhydride concentration

by the addition of either acetic anhydride or pyridine. The total volume of the acetylation mixture was kept constant at 1690 cc. After stirring the pulp in the acetylation mixture for five minutes with the Lightnin mixer, the jar was placed on the rotating mixer for the desired number of minutes, and at the end of this time the acetylation mixture was removed from the pulp by suction on a Buchner funnel. Ten minutes were allowed for the removal of the acetylation mixture, and the time of acetylation was taken as the elapsed period from the addition of the acetylation mixture to the jar until the end of the ten-minute drainage time. In the short acetylation periods, there was no formation of red color in the acetylation mixture; therefore, the washing with pyridine was omitted. Instead, the material was washed immediately with alcohol and ether and then dried in the same way as were the pulps of higher acetyl content.

The method of acetylation of the Mitscherlich pulp was the same as that for the rag stock with the exception that pulp equivalent to 130 grams of oven-dry weight was used and the total volume of the acetylation mixture was 3380 cc. The acetylation was carried out in a one-gallon, glass-topped fruit jar; because this jar could not be placed on the stirrer, the jar was shaken by hand. On the longer acetylation times the jar was placed in the water bath at 40° C. after a few minutes of shaking by hand.

Table III gives a summary of the conditions of acetylation used in this study and the acetyl contents resulting from the materials.

TABLE III

SUMMARY OF ACETYLATING CONDITIONS AND ACETYL CONTENTS OF CELLULOSIC MATERIALS

Concn. of Acetic Anhydride, %*	Total Acetylating Time	Acetyl Content, %
	RAG STOCK	
5.0	30 minutes	1.24
7.5	30 minutes	2.08
9.6	30 minutes	3.11
19.2	30 minutes	4.42
38.4	35 minutes	5.31
38.4	70 minutes	6.85
38.4	7 hours	8.16
38.4	24 hours	10.36
38.4	5 days	14.76
38.4	10 days	18.24
38.4	30 days	22.92
38.4	41 days	23.40
	MITSCHERLICH PULP	
2.5	70 minutes	2.61
5.0	70 minutes	4.05
7.5	70 minutes	6.75
38.5	45 minutes	7.95
38.4	10 hours	12.98
38.4	3 days	15.37
38.4	12.5 days	18.47
38.4	41 days	23.26

*Concentration of acetic anhydride in acetylation mixture expressed as percentage by volume.

The results show that the rate of acetylation of the Mitscherlich pulp was slightly faster than that of the rag stock at low acetyl content, but at high acetyl contents the time required to introduce a given acetyl content was practically the same with both materials.

ACETYL DETERMINATION

After a thorough investigation of the methods of determining the acetyl content of cellulose acetates, Genung and Mallatt (24) found a modification of the Eberstadt method to be the most accurate. In this method the cellulose acetate is saponified with alcoholic sodium hydroxide after swelling in 75 per cent ethanol. It was found that the swelling could be eliminated in many cases. Using 0.25 N sodium hydroxide and a temperature of not over 35° C., the time necessary for complete saponification was 16-24 hours; and under these conditions the cellulose constituent is not degraded. The method has a precision of ± 0.1 per cent acetyl and an accuracy of ± 0.2 per cent acetyl.

The procedure used in this investigation (that of Genung and Mallatt with minor modifications) was as follows: One-half gram of oven-dry material was placed in a 250-cc. Erlenmeyer flask, 25 cc. of 75 per cent ethanol added, and the sample digested for an hour in a water bath at 50 to 60° C. Twenty-five cc. of 0.5 N sodium hydroxide were added from a pipette, the flask tightly stoppered, and the contents digested in the water bath at 50-60° C. for 15 minutes. The samples were then allowed to stand for 30 hours at room temperature with occasional shaking. At the end of this time the sides of the flask were washed down with a small amount of distilled water, two drops of one per cent phenolphthalein and, subsequently, depending upon the acetyl content of the material, 50 or 100 cc. of 0.1 N hydrochloric acid were added. The excess alkali was then titrated with 0.1 N hydrochloric acid. After the solution had become colorless,

there was usually some alkali left adsorbed on the cellulose, and the mixture was allowed to stand for several hours with occasional shaking and addition of acid to neutralize these last traces of alkali. All determinations were run in triplicate.

$$\% \ CH_3COO = (0.0215)(\text{cc. of } 0.5 \ \underline{N} \ NaOH)(100)/\text{wt. of sample}$$

BEATING OF PULPS AND TESTING OF HANDSHEETS

After a careful consideration of the various laboratory devices available for strength evaluation of pulps, the Lampén mill was chosen as the most desirable one to use for this study for the following reasons:

(1) It has been thoroughly tested and found to be reproducible and to correlate well with results obtained by beating in the mill. Harrison (25) has given a thorough discussion of this device.

(2) It requires only a 24-gram charge for each beating interval.

(3) The procedure is fairly rapid.

The procedure for beating given in the Second Report of the Pulp Evaluation Committee of the Technical Section of the Paper Makers' Association of Great Britain and Ireland (26) was followed, with the exception that, after disintegration, the pulp was concentrated by filtering through a filter paper on a Büchner funnel instead of using a screen thickener. With the Mitscherlich pulps a charge of eighteen grams was used, but the consistency was kept at

three per cent. All materials were soaked in water for at least four hours before beating.

Two methods are in general use for the strength evaluation of pulps. In the first a strength development curve is obtained by subjecting the pulp to various degrees of beating. This method yields valuable information on the strength of the pulp developed at any given beating interval, and also furnishes an insight into the rate of development of strength characteristics. This method was used with the acetylated Mitscherlich materials with beating intervals of 0, 5, 10, 20, and 40 minutes.

The second method is to beat all of the materials to be compared for one standard beating time under fixed conditions. In conjunction with this method, in addition to the one beating interval, sheets for strength evaluation are frequently made from the unbeaten material. The chief advantage of this method is that it is economical with regard to both time and material. At the time the rag stock was acetylated there was available only a limited amount of pyridine, and enough material was not acetylated to allow a complete beating curve. Tests on the unbeaten materials were omitted, because of the difficulty of forming uniform sheets of unbeaten rag stock, especially after it has been acetylated. A beating curve was run on the unacetylated rag stock at 0, 15, 30, 45, and 65-minute beating intervals, the results of which are given in Table IV. It is seen from these data that in the Lampén mill, as in other laboratory testing equipment, strength is not developed in rag stock to as great an extent as it is in the mill. The bursting strength passed through

a maximum value after 15 minutes of beating, and the tensile strength passed through a maximum value after 45 minutes of beating. Any period in this range could have been used for beating the acetylated rag stocks. The 45-minute interval was chosen, and a check run was made at this beating interval on the unacetylated rag stock. These results are also given in Table IV.

In this study the sheets were formed, pressed, dried, and conditioned according to TAPPI Standard methods. Drainage time was measured at the time the sheets were made, and the sheets were tested according to TAPPI Standards for basis weight, caliper, and tearing, bursting, and tensile strengths.

Trimmings from the tested sheets were dried in order to determine the moisture content, and the basis weight was calculated on a 25x40--500 oven-dry basis. On the acetylated material the basis weight was calculated to the acetyl-free basis to give a comparison of equal numbers of fibers. The strength values were divided by the basis weight in order to reduce them to a common basis for purpose of comparison.

TABLE IV

STRENGTH VALUES ON UNACETYLATED RAG STOCK

Beating time, min.	0	15	30	45	45 (check)	65
Freeness, cc.	665.0	630.0	560.0	495.0		410.0
Drainage time, sec.					15.85	
Basis weight, oven-dry	44.45	40.0	43.0	42.5	43.35	45.0
Caliper	5.6	4.7	4.7	4.3	4.29	4.45
Apparent density, oven-dry	7.94	8.51	9.20	9.89	10.1	10.1
Bursting strength	23.2	26.6	27.1	24.2	24.3	21.4
(Burst/basis weight)100	52.3	66.5	62.8	57.0	56.1	47.6
Tearing strength	199.0	159.0	160.0	137.0	137.0	100.0
Tear/basis weight	4.49	3.97	3.70	3.22	3.16	3.04
Tensile strength	3.17	4.28	7.97	8.36	8.39	8.54
(Tensile/basis weight)100	7.09	10.7	18.45	19.65	19.35	19.00

THE EFFECT OF ACETYLATION ON THE PAPERMAKING PROPERTIES OF RAG STOCK

The strength of a sheet of paper depends upon many factors, but the predominant factors in a handsheet for strength evaluation are the length and strength of the individual fibers and the bonding forces between the fibers. In weak pulps, the strength of the individual fibers plays a more important role than it does in stronger pulps, where the bonding force between the fibers is of more importance. As mentioned earlier, Obermanns (20) found that when a pulp is over-bleached--that is, when the individual fibers have been degraded--the pulp develops strength at a faster rate in the beater, but in spite of this greater ease in developing bonding strength, the strength of the sheet is lower because of the degraded condition of the individual fibers.

Measurements of bursting, tearing, and tensile strengths are the most common tests used in evaluating the strength of handsheets. The values obtained in these tests depend upon several factors, but it is generally agreed that with a material of strong individual fibers, the bonding strength between the fibers is the primary factor in both bursting and tensile strengths and is of importance to a lesser degree in tearing strength. Any changes produced in the bonding strength of a pulp by some treatment that did not degrade the pulp should be revealed by the bursting and tensile strengths of sheets made from the beaten pulp.

Bletzinger pointed out that, in covering up the hydroxyl groups of cellulose by acetylation, the strength of the individual

fibers might possibly be weakened by two causes. (1) The fiber might be degraded by shortening the chains in the cellulose, or (2) the tensile strength of the individual fiber might be weakened by disturbance of the internal forces that hold the structural elements in the fiber together. It was shown by Bletzinger that with the method of acetylation used, neither of these weakening actions took place. Chain-length determinations on the material before and after acetylation showed that no degradation had taken place during acetylation. Likewise, tensile strength determinations on individual cotton fibers before and after acetylation showed no change in the tensile strength after acetylation. Therefore, any changes that take place in the bursting and tensile strengths of the material upon acetylation must be due to a change in the bonding forces between the fibers.

The rag stocks acetylated in this study were beaten in the Lampén mill for 45 minutes. The strength results obtained are given in Table V and Figure 1.

DISCUSSION OF STRENGTH PROPERTIES

Bletzinger found that, when 6.1 per cent acetyl had been introduced into rag stock, there was a small increase in bursting strength. In order that this strength increase might be more carefully studied, eight samples with acetyl contents varying from zero to ten per cent were prepared in the present study. The data of Table V and Figure 1 show that the maximum increase in strength properties occurred at 3.1 per cent acetyl content and that in the present study the 6.1 per cent acetyl content material of Bletzinger was above the

FIGURE 1

THE EFFECT OF ACETYLATION ON THE PAPER-MAKING PROPERTIES OF RAG STOCK

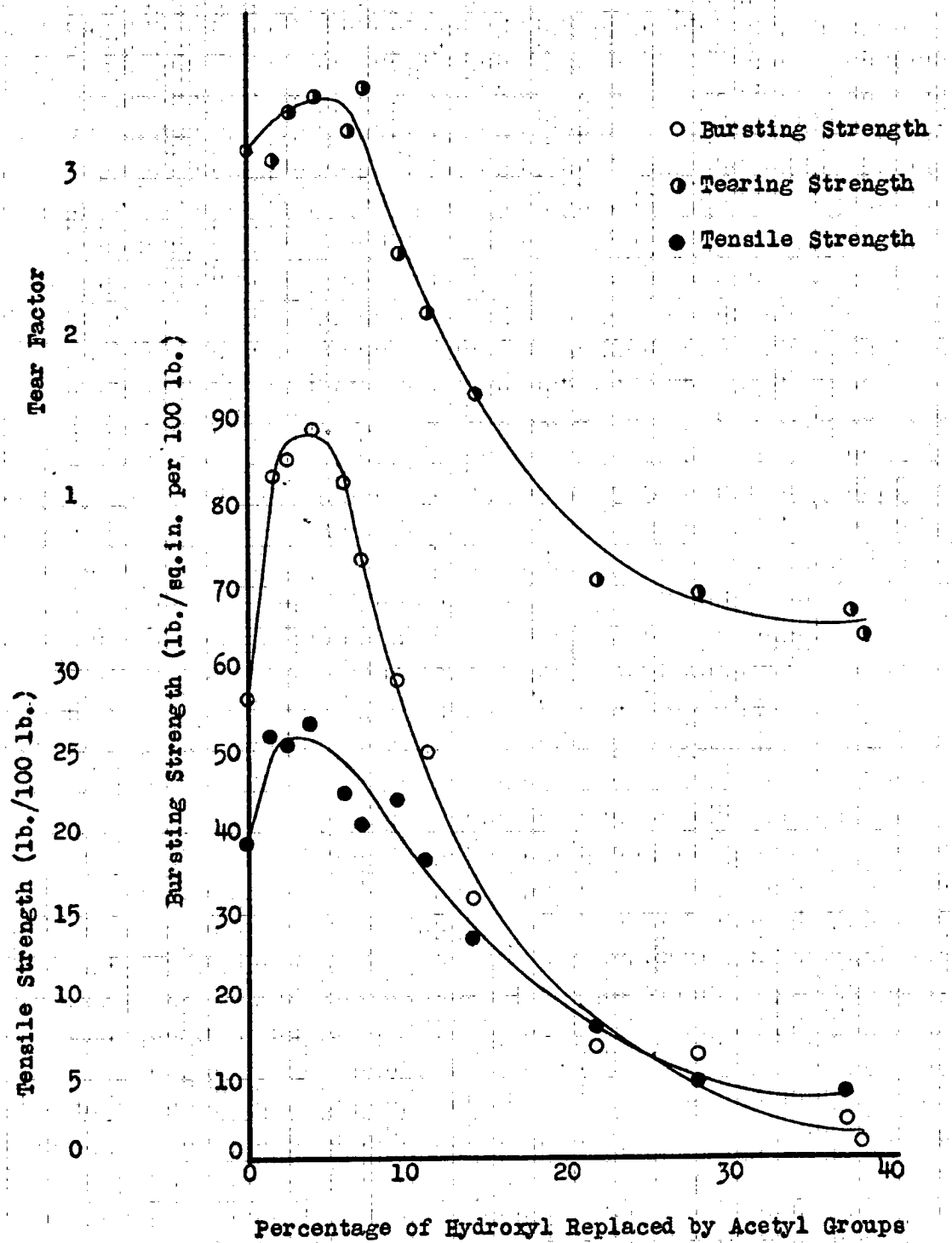


TABLE V A

SUMMARY OF STRENGTH RESULTS OF ACETYLATED RAG STOCKS

Acetyl Content %	Hydroxyl Groups Covered %	Caliper 0.001 in.	Basis Weight	Apparent Density B. W. / Caliper	Bursting Strength (lb./sq.in.)/ 100 lb.	Tear Factor	Tensile Strength lb./ 100 lb.
0.00	0.00	4.21	43.35	10.10	56.06	3.160	19.35
1.24	1.58	5.53	45.41	8.21	82.35	3.060	25.63
2.08	2.67	4.32	43.24	10.10	83.72	3.307	24.81
3.11	4.03	5.06	54.27	10.72	86.79	3.372	25.79
4.42	6.16	4.75	47.08	9.92	79.22	3.122	21.33
5.31	7.03	4.33	45.21	10.44	69.45	3.340	19.51
6.85	9.23	4.30	44.79	10.42	54.25	2.360	20.70
8.16	11.14	5.15	60.60	11.77	46.04	1.997	16.80
10.36	14.47	4.31	43.13	10.61	28.74	1.502	12.10
14.76	21.66	5.66	52.77	9.33	11.88	0.463	6.89
18.24	27.88	6.33	52.73	8.34	10.80	0.363	4.22
22.92	37.09	9.20	78.07	8.49	3.84	0.273	3.39
23.40	38.09	6.48	53.87	8.31	1.85	0.163	----

TABLE V B

SUMMARY OF STRENGTH RESULTS OF ACETYLATED RAG STOCK CALCULATED TO CELLULOSE BASIS

Acetyl Content %	Hydroxyl Groups Covered %	Drainage Time sec.	Caliper 0.001 in.	Basis Weight	Apparent Density B. W. / Caliper	Bursting Strength (lb./sq.in.)/ 100 lb.	Tear Factor	Tensile Strength lb./ 100 lb.
0.00	0.00	15.9	4.21	43.35	10.10	56.06	3.160	19.35
1.24	1.58	27.2	5.53	44.86	8.11	83.36	3.096	25.94
2.08	2.67	16.5	4.32	42.36	9.65	85.44	3.375	25.56
3.11	4.03	19.7	5.06	52.54	10.38	89.64	3.481	26.64
4.42	6.16	13.7	4.75	45.00	9.42	82.89	3.271	22.31
5.31	7.03	16.2	4.33	42.87	9.90	73.01	3.522	20.51
6.85	9.23	19.0	4.30	44.79	9.70	58.39	2.527	22.18
8.16	11.14	23.9	5.15	55.76	10.83	50.04	2.170	18.25
10.36	14.47	14.1	4.31	38.77	8.99	31.90	1.671	13.46
14.76	21.66	8.0	5.66	45.16	7.98	13.88	0.537	8.06
18.24	27.88	6.2	6.33	43.40	6.86	13.13	0.440	5.14
22.92	37.09	5.1	9.20	60.33	6.45	4.97	0.354	4.39
23.40	38.09	4.9	6.48	41.56	6.41	2.41	0.212	----

maximum strength value. With a material of 4.25 per cent acetyl content, Eletsinger obtained a material of lower strength properties than with his material of 6.1 per cent acetyl content; however, this material was prepared in an acetylation time of only ten minutes in an acetylation mixture containing 38.4 per cent by volume of acetic anhydride, and it is unlikely that a uniform product was produced in this very short acetylation time.

The results obtained in this investigation show that upon acetylation of rag stock there was an increase in bursting strength over that of the unacetylated material in the range of zero to seven per cent acetyl content, with a maximum increase of 78 per cent at an acetyl content of 3.1 per cent. Beyond the maximum value the bursting strength fell rapidly until about 15 per cent acetyl had been introduced, when the material had very little strength. Beyond this point the strength continued to fall only slowly to a value of 2.4 points per hundred pounds at an acetyl content of 23.4 per cent.

The tensile strength of the acetylated rag stock followed the same general trend as the bursting strength. There was an increase in tensile strength over that of the unacetylated material in the range of zero to seven per cent acetyl content, with a maximum increase of 39 per cent in the range of 1.0 to 4.5 per cent acetyl content. Beyond 4.5 per cent acetyl content there was a rapid decrease in tensile strength until an acetyl content of about 15 per cent had been reached, and beyond this point there was a steady decrease to a tensile strength value of 4.4 pounds per 100 pounds basis weight at an acetyl content of 22.9 per cent.

The tearing strength of a sheet does not depend upon fiber-to-fiber bonding nearly so much as do bursting and tensile strengths. In the material used in this investigation, however, there was an increase in tearing strength over that of the unacetylated material of about ten per cent in the range of two to five per cent acetyl content. Beyond six per cent acetyl content the tearing strength showed the same trend as the bursting and tensile strengths, with a rather rapid decrease to about 15 per cent acetyl content, and a more gradual decrease beyond this point. At an acetyl content of 23.4 per cent, the tear factor was 0.21.

These results (which in general confirm those obtained by Bletzinger) show that, with the introduction of a small amount of acetyl content into the rag stock, some change took place that greatly increased the bonding strength in the sheets made from the beaten material. With the introduction of more acetyl content, these strength properties decreased rapidly until the sheet had very little strength at 15 per cent acetyl content. Beyond 15 per cent acetyl content the decrease in strength properties continued further until 23.4 per cent acetyl content had been reached, which was the maximum amount introduced in 41 days of acetylation.

DISCUSSION OF DRAINAGE TIME

The ease with which water will drain from a pulp is usually associated with the extent to which the material has been beaten, and is considered by the papermaker as a measure of "hydration"--that is, the ability of the pulp to bond when it is made into a sheet. The

drainage properties, however, depend upon other factors besides hydration, fiber length being of considerable importance. There are many devices for measuring this property, and the results are expressed as freeness, wetness, drainage time, rate of drainage, etc. Unfortunately, there is no correlation between these devices in many cases. Indeed, Reed (27) found that with several pulps one device would indicate a free pulp and another a slow pulp. It is not surprising, then, that whereas Bletzinger's results show the freeness to be correlated with the strength properties of acetylated rag stock, Brown and Harrison (3) found no correlation of the strength properties of acetylated kraft pulp and wetness; likewise, in the present study no correlation of drainage time and the strength properties of acetylated rag stock could be established.

Bletzinger found a minimum in freeness at 6.1 per cent acetyl content, and then an increase in freeness with the introduction of additional acetyl content. This minimum in freeness was at the same acetyl content at which the maximum strength properties were noticed, and as the strength of the materials decreased, the materials became more free. In the study of Brown and Harrison little correlation between acetyl content and wetness is observed until 30 per cent combined acetic acid, corresponding to 21.5 per cent acetyl, had been introduced into kraft pulp. Beyond this acetic acid content the materials were all very free, and the strength properties were all very low.

In the present study TAPPI drainage time was used, and at low acetyl contents no correlation was found between drainage time

and either acetyl content or strength properties. Beyond ten per cent acetyl content, however, the drainage time steadily decreased with increasing acetyl content and decreasing strength.

DISCUSSION OF APPARENT DENSITY

Doughty (7) has shown that there is a straight-line relationship between the solid fraction and the tensile strength of handsheets, indicating that the strength of the sheet depends upon the number of fiber-to-fiber contacts. Plotting the bursting and tearing strengths against solid fraction gave curves similar to those obtained by plotting these properties against beating time. These results strongly support the theory of Campbell that the purpose of beating is to reduce the fibers to such a state that they can be drawn into intimate contact by the surface tension of the water operative between the fibers.

The work of Doughty indicates that the attractive forces per unit of fiber-to-fiber contact of a pulp are the same, and to increase the strength of the sheet we need only to increase the number of such contacts. If two similar materials of the same degree of polymerization have been beaten to the same degree, and if the materials have the same number of fiber-to-fiber contacts, as measured by equal apparent densities, it is logical to assume that the attractive or bonding forces in each material are the same if sheets of the two materials have the same strength properties. However, if the attractive forces of one of the materials were greater than those of the other, this material should have greater strength at any given apparent density than the material with lower attractive forces.

In his study with acetylated rag stocks, Bletzinger prepared three sets of sheets from each beaten material and pressed these sheets at different pressures to obtain different solid fractions. He found that, with increasing acetyl content and decreasing strength properties, the sheets had lower apparent densities--that is, there was less fiber-to-fiber contact. However, when the data for the sheets pressed to different solid fractions were extrapolated to give strength values of the acetylated materials at constant solid fraction, there was an appreciable decrease in strength at the same apparent density with increasing acetyl content. Therefore, the covering of the hydroxyl groups had reduced the attractive forces causing the fiber-to-fiber contacts.

The results of the present investigation confirm Bletzinger's results, for it was found that, with the material of higher acetyl content, there was, with increasing acetyl content, a decrease in apparent density, indicating that the attractive forces had been reduced for each fiber-to-fiber contact, but the decrease was not proportional to the decrease in tensile strength. At the lower degrees of acetylation, where the greatly increased strength properties were noted, there was no correlation at all between apparent density and strength properties, indicating that in these materials widely different attractive forces were operative at the points of fiber-to-fiber contact.

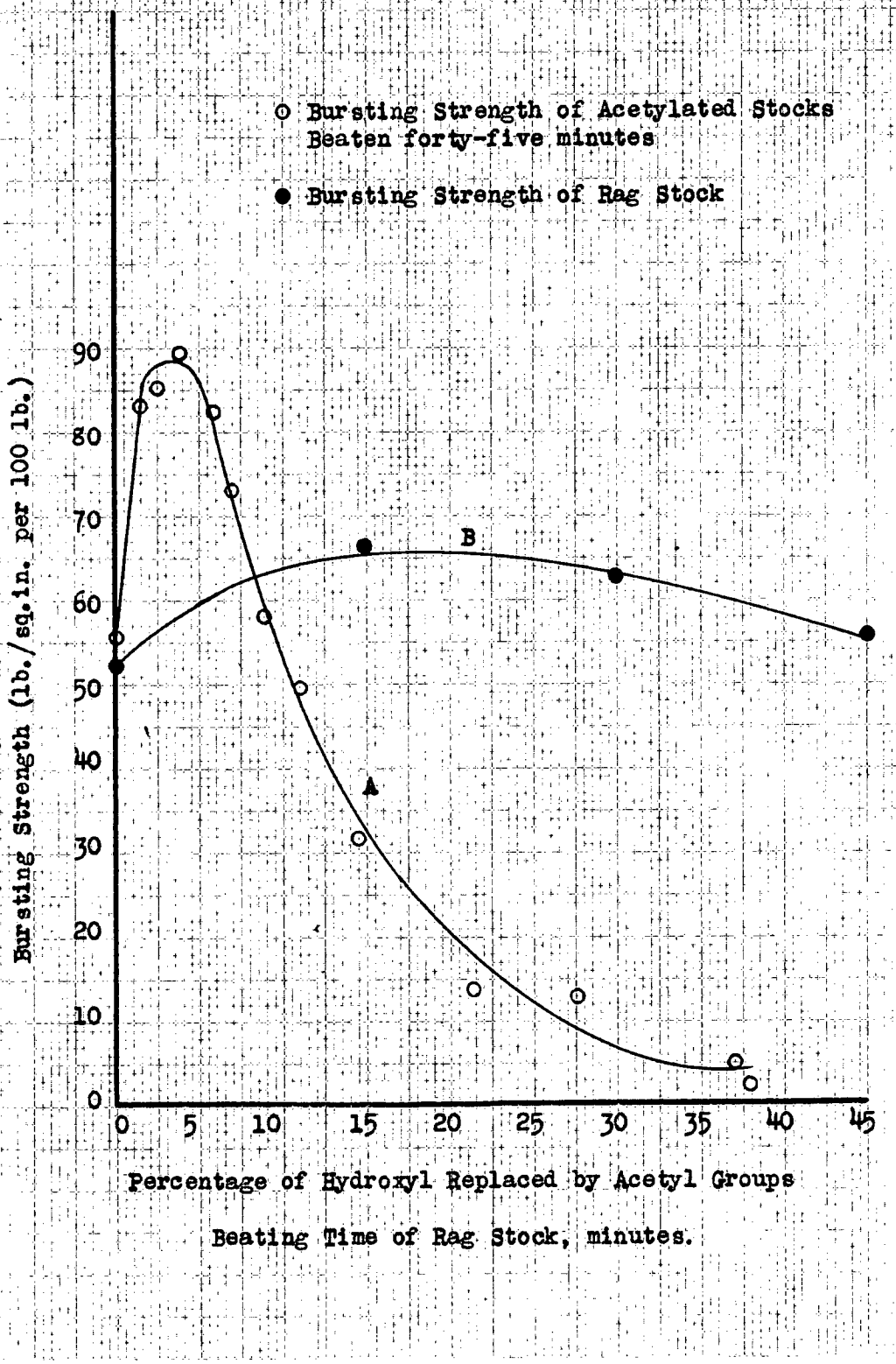
GENERAL DISCUSSION

The method of strength evaluation used in this investigation might be regarded as somewhat questionable, for the acetylated rag stocks had widely different strength properties, and it could not be expected that only one beating interval would give a true picture of the strength characteristics of these materials, because different materials develop their strengths at different rates. However, the method used can be partially justified by Brown and Harrison's observation--namely, that kraft pulps acetylated to different degrees did not have widely different rates of development and that these rates, after the materials had developed their properties, were fairly constant over a wide range of beating. The beating time used in the present investigation should then have been sufficient to develop maximum strength in all of the materials used.

An examination of the strength data for the unacetylated rag stock and for the acetylated materials justifies the conclusion that the strength differences noted in the acetylated materials could not have possibly been due to differences in the behavior of the materials in the beater. These data are plotted in Figure 2. Curve A is a plot of the bursting strength of the acetylated rag stock against its acetyl content and curve B is a plot of the bursting strength of the unacetylated rag stock against the beating time. It is seen from these data that the strength properties developed in the acetylated materials of low acetyl content were very much better than those developed in the unacetylated material at any beating interval. Thus, the changes in strength properties arising from acetylation must have

FIGURE 2

STRENGTH RESULTS OF ACETYLATED RAG STOCK
COMPARED WITH RAG STOCK STRENGTH RESULTS



been due to changes brought about by the covering of hydroxyl with acetyl groups.

There are two factors that must be considered in explaining the decrease in strength in the acetylated material of high acetyl content. As mentioned earlier, the work of Kress and Bialkowsky has shown that the beating medium must wet the fibers if strength is to be developed upon beating. If the fibers are not wet and not swelled by the medium, the normal beating actions do not take place, and when the beaten material is formed into a dry sheet—that is, when the beating medium is removed—the fibers are not drawn into sufficiently intimate contact. With such fibers there are, therefore, fewer fiber-to-fiber contacts, which results in a decrease of apparent density and of strength of the sheet. On the other hand, as more of the hydroxyl groups of the cellulose are covered by acetylation, the material becomes more hydrophobic and hence is wet less by water; thus, the end effect ought to be practically the same as when a nonswelling medium is used with unacetylated fibers.

It was observed that, as the acetyl content of the materials was increased to more than 15 per cent, the fibers became so water-repellent that they floated on the surface of the water. Likewise, when the 15 per cent material was beaten in water, it was only slightly wet and swelled little by water, and the fiber-to-fiber contacts were less; therefore the apparent density of the sheet was lower. However, this decrease in apparent density was not great enough to account for the decrease in strength properties, and thus the attractive forces

of the hydroxyl groups at each fiber-to-fiber contact must have been reduced by covering the hydroxyl groups.

It would seem logical that, at the lower degrees of acetylation, these two factors would have an effect, but to a lesser extent. The results of Bletzinger's and of this investigation show, however, that very different actions have taken place. Instead of a decrease in strength properties, there was a large increase. This increase in strength properties does not correlate with apparent density, so apparently there has been a large increase in the attractive forces per unit fiber-to-fiber contact. It appears that the introduction of a small percentage of acetyl groups has greatly increased the number of hydroxyl groups available for bonding per unit area.

HYGROSCOPIC STUDY OF ACETYLATED RAG STOCK

As pointed out earlier, Sheppard and Newsome (1 and 2) found that, if some of the hydroxyl groups of cellulose were covered by acetyl groups, the water-binding property of the material was decreased in proportion to the number of hydroxyl groups covered. Moreover, the results of Bletzinger's and of the present investigation have shown that, as the hydroxyl groups of cellulose are covered by acetyl groups beyond eight per cent acetyl content, the strength properties of the materials decrease as the number of hydroxyl groups covered increases. It is logical, then, to assume that there should also be a correlation between the strength properties of the acetylated materials and their water-binding properties.

In the present investigation an increase of 78 per cent in bursting strength and an increase of 29 per cent in tensile strength were obtained with rag stock of an acetyl content of 3.1 per cent. If the strength properties in cellulose arise from the bonding between hydroxyl groups and if, as postulated earlier, the introduction of a small amount of acetyl content into the fiber increases the number of hydroxyl groups available for bonding, one would expect also to find an increase in the water-binding properties at such low degrees of acetylation.

In order to ascertain if there actually exists a relation between the water-binding properties and the strength properties of acetylated materials, the water-binding capacities of the materials of acetyl contents from zero to 10.36 per cent were determined.

STUDY OF THE WATER-BINDING PROPERTIES OF ACETYLATED RAG STOCKS

Two methods for ascertaining the water-binding properties of the acetylated materials and for comparison with the unacetylated material were used.

(1) The amount of water sorbed by the materials from the air at various relative humidities was determined by ascertaining the increase in weight of the cellulosic materials directly.

(2) An attempt was made to determine the amount of water sorbed by the materials from liquid water itself by an indirect method based upon changes of the dielectric constant of dioxane with the introduction of various amounts of water.

APPARATUS FOR HYGROSCOPIC STUDY (Method 1)

The chamber for the hygroscopic study consisted of a double-walled box with insulating material between the walls, and with a double glass observation window in front. The box was approximately thirty inches on a side, had a removable top, and had no bottom. The box rested on a rubber-tubing seal over a large enameled tray on top of a table. Six inches up from the bottom of the box was a half-inch meshed wire floor to separate the rest of the box from the tray. Manipulation of samples was made possible by two holes, each seven inches in diameter, cut in the front of the box just above the screen floor. Into these holes were glued arms of vaporproof, rubberized cloth with rubber gloves attached. This box has been constructed by the Physics Department of the Institute for their instrumentation studies.

The humidity of the box was controlled by placing various salts covered with their saturated solutions on the enameled tray, and the salts were changed by lifting one side of the box and sliding the tray out. Circulation of air was provided by a fan in front of which was a deflector to pass the air stream over the tray of saturated salt solution. Heating was accomplished by two fifty-watt light bulbs on the two sides of the fan, and the temperature was controlled by means of a thermoregulator. A wet and a dry bulb thermometer were kept in the humidity box to be used in determining relative humidity; before use, the wick of the wet bulb thermometer was wet with distilled water from a stoppered bottle kept in the box.

The sample containers were small buckets one inch in diameter and one and a half inches high, made from 200-mesh copper wire. The buckets were suspended by handles from hooks on a wooden frame which rested on the wire floor. This type of container allowed good circulation of air around the samples, and the buckets could be transferred to and from the balance easily.

The samples were weighed on an analytical balance located on top of the box. The left pan of the balance was removed, a hole drilled in the bottom of the balance, and a stainless steel wire hooked to that side of the balance. The wire extended into the box through a small hole in the top of the box, and the free end of the wire was hooked to receive the sample buckets. Weights were suspended on the left side of the balance to compensate for the difference in weight between the right weighing pan and the wire.

PROCEDURE

The amount of water that a cellulosic material will take up from the air at any given relative humidity not only depends upon the nature of the material, but also upon its previous history with regard to absorption and desorption. To avoid differences from the latter cause, a sample of each material was taken after it was removed from the acetylation mixture and washed with alcohol and ether, but before all of the ether had been sucked out of the pad. This sample consisted of small shreds of pulp taken from various parts of the pad. The sample was divided into two parts, which were put into two of the copper wire buckets and stored in a vacuum desiccator over calcium

chloride to remove the ether and keep the samples dry. It was thought that this procedure would produce samples whose only differences in hygroscopicity would depend upon the nature of the materials themselves.

After several samples had been dried and stored for several days in this manner, the containers were transferred to the rack in the humidity chamber, which had been brought to a low humidity. The samples were left at this humidity for several hours, when two different samples were weighed. A few hours later the same two samples were weighed again, and if no change in weight had taken place, it was assumed that the samples were at equilibrium, and all of the samples were then weighed. It was found that, at the lower humidities, the samples came to equilibrium in a few hours, whereas at higher humidities as much as a day was required. After the samples had been weighed at a given humidity, the salt in the tray was changed, and the samples allowed to come to equilibrium at the new humidity. The fan was cut off while weighings were being made and the salt solutions were being changed.

The hygroscopic measurements were made at 30° C. so that the temperature of the chamber would always be above that of the room and could be controlled by the heating element, as the box was not provided with a method of cooling.

Two empty buckets were weighed at each humidity to see if there was any change in their weight. No change in the weights of the containers was observed except at 100 per cent relative humidity. It

was found that it was impractical to make measurements at this high relative humidity, not only because of a small amount of condensate on the buckets, but also because the wire running from the balance to the inside of the box was at a temperature lower than the temperature inside the box, and condensation took place on this wire.

This method has a precision of ± 0.2 per cent water bound.

DISCUSSION OF RESULTS

The results of the hygroscopic study are given in Table VI. In Figure 3 hygroscopic data at 20, 40, 60, 80, and 100 per cent relative humidities, obtained by interpolation and extrapolation of the measured values, are plotted against acetyl content; the strength data obtained on the materials plotted against acetyl content are also given.

Inspection of Figure 3 shows that there is a good correlation between the strength properties and the hygroscopic properties of the materials. As acetyl was introduced into the rag stock, there was, as has been shown earlier, an increase in the strength properties of the materials over that of the unacetylated rag stock in the range of zero to seven per cent acetyl content, with the maximum strength increase at 3.1 per cent acetyl content. Beyond seven per cent acetyl content, the strength of the material fell to values below those of the unacetylated rag stock. The hygroscopicity of the acetylated rag stocks followed the same trends as the strength properties. In the range of zero to seven per cent acetyl content the water bound at any given relative humidity was greater than that

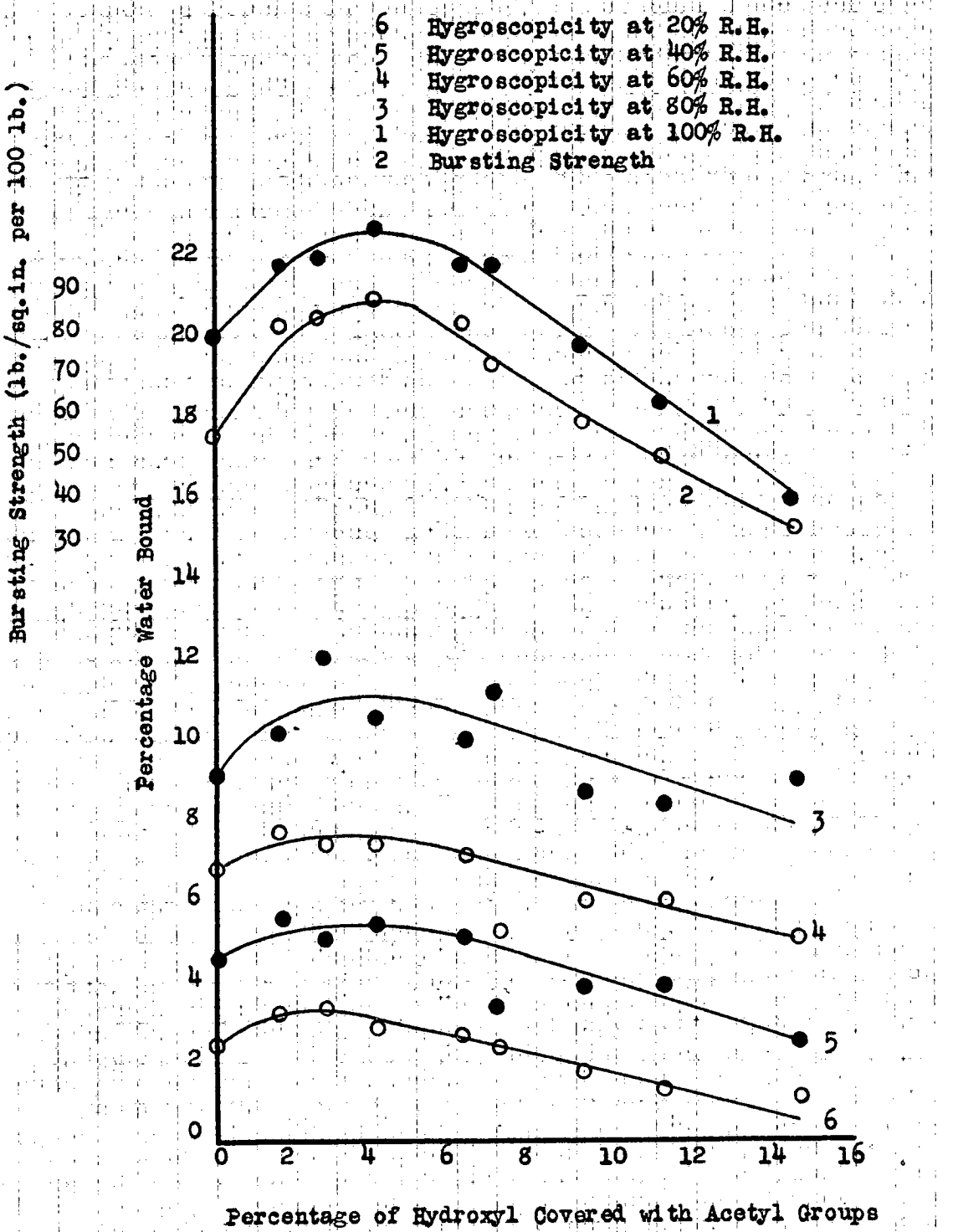
TABLE VI

RESULTS OF HYGROSCOPIC STUDY ON ACETYLATED RAG STOCKS

Relative Humidity %	Percentage of Water Bound at Increasing Relative Humidity — Acetyl Content of Samples, %								
	0.00	1.24	2.08	3.11	4.42	5.31	6.85	8.16	10.36
14.3			2.48			1.86			1.19
27.4	3.18	4.06		3.75	3.38		2.47	2.54	
45.9	5.30	6.28		6.07	5.72		4.71	4.49	
46.4			5.34			2.82			2.36
58.2	6.36	7.40		7.23	6.83		5.77	5.76	
62.1			7.59			5.88			5.58
78.1			10.77			10.21			8.80
81.8	9.29	10.70		10.73	10.72		19.22	19.08	
97.4	18.53	20.50		21.27	20.23		18.73	17.58	
98.5			21.06			20.68			17.14

FIGURE 3

HYGROSCOPIC RESULTS ON ACETYLATED RAG STOCKS COMPARED WITH THEIR BURSTING STRENGTH



bound by the unacetylated rag stock, with a maximum amount of water bound at 3.1 per cent acetyl content. In the materials of acetyl content greater than 3.1 per cent, the amount of water bound fell below that bound by the unacetylated rag stock.

The direct relation which thus exists between the water-binding capacity, the strength properties, and the acetyl content of acetylated rag stocks indicates that, upon the introduction of a small amount of acetyl content into the rag stock, the internal structure of the fiber is opened up to leave fewer hydroxyl groups mutually satisfying each other, so that more are left free for the binding of water. When such materials are beaten and made into sheets, these additional hydroxyl groups may be expected to serve to form a stronger bond at each fiber-to-fiber contact so that a stronger sheet is produced.

STUDY OF WATER BOUND BY ACETYLATED RAG STOCK IN LIQUID WATER (Method 2)

The method described above gives the amount of water that is bound by cellulosic materials from the air at different relative humidities. However, even the amount of water bound at 100 per cent relative humidity is not a measure of the amount of water that is bound when the cellulosic material is in contact with liquid water itself. According to von Schröder's paradox (25), the amount of water bound by the material from liquid water should be greater than that bound from the saturated vapor. It was therefore thought pertinent to determine the amount of water bound from liquid water by the acetylated rag stocks.

As mentioned earlier, Froundjian and Jayme (16) have developed a method for measuring the water bound by cellulosic materials in contact with liquid water. By the use of this method they showed that a pulp of eight to ten per cent methoxyl content bound 15.9 per cent water, whereas the unmethylated material bound only 10.23 per cent water. The methylated materials also showed greatly increased strength properties. This indicates that the internal structure of the cellulose has been greatly opened, thereby freeing additional hydroxyl groups for water binding and fiber-to-fiber bonding.

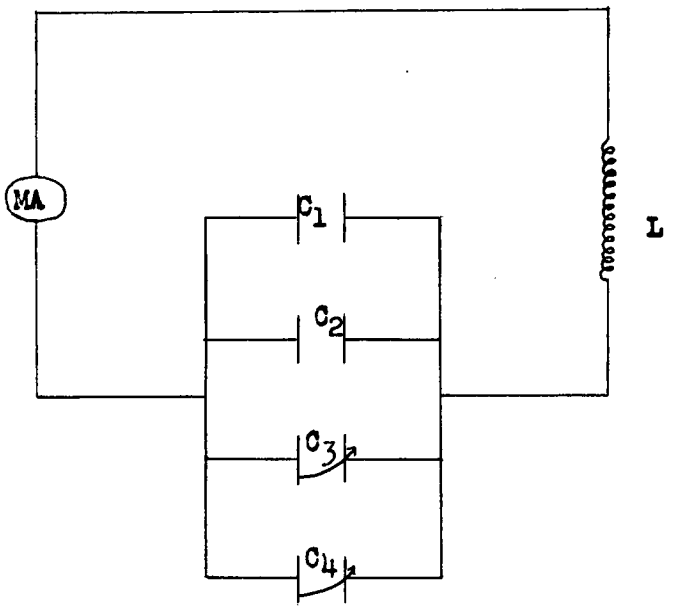
In the method of Froundjian and Jayme, soaked, disintegrated pulp is filtered and the pad quartered. Two portions are dried for total moisture content. The other two portions are soaked in dioxane, which is said to remove only the capillary water. The dielectric constant of the aqueous dioxane is then determined using a commercial dielectric constant apparatus, and the water content of the dioxane is ascertained from a calibration curve prepared from dioxane containing known amounts of water. The difference in the total moisture content of the pulp and the water in the dioxane gives the amount of water regarded to be actually bound by the cellulose.

APPARATUS

Because a commercial dielectric constant apparatus was not available, a device was built with the assistance of the Physics Department that could be calibrated with the water-dioxane mixtures--that is, on the basis of changes in the dielectric constant of the dioxane occurring with the introduction of water. The apparatus con-

sisted of an oscillator and a receiver, which had the measuring cell in parallel with the tuning condensers so that the point of tuning on the dial varied with the dielectric constant of the material in the cell.

The oscillator was the 30-watt push-pull Hartley oscillator described by Tyndt (29). The receiver is shown diagrammatically below.



C_1 = 0.0005-microfarad 5000-volt mica condenser.

C_2 = measuring cell.

C_3 = 0.0005 microfarad variable condenser, referred to below as the large condenser.

C_4 = 0.0005 microfarad variable condenser with three plates, referred to below as the Vernier condenser.

MA = 0-1 milliamperes, rectifier type ammeter shunted by a seven-inch coil of #14 bare copper wire.

L = 44 turns of #14 cotton-covered wire on a 2.5-inch glass tube core.

The plates of the condenser cell, C_2, were of brass with polished faces and were two inches in diameter. The plates were separated by four small pieces of microscopic cover glass cemented together by porcelain cement. The bottom plate was supported on three short brass legs, and a glass rod was cemented to the top plate to act as a handle. Flexible leads were soldered to the two plates. The container for the condenser was a glass weighing bottle with a diameter of 3.75 inches and 1.125 inches high.

USE AND CALIBRATION OF APPARATUS

Before measurements were made, the oscillator was put into operation and allowed to warm up for a minute. Then the dioxane-water mixture was placed in the cell and the dial of condenser C_3 moved until deflection of the ammeter needle indicated that the receiver was almost in tune. This condenser was then adjusted so that the indicator was exactly over one of the nearest divisions, and the receiver was then tuned to resonance, as indicated by maximum deflection of the ammeter needle, with the Vernier condenser (C_4). Ten readings were taken on the Vernier condenser with each sample to eliminate small errors that might arise from inexact tuning.

To calibrate the apparatus, known dioxane-water mixtures were used. When a sample had been placed in the cell, ten readings were taken on the Vernier condenser (C_4) at one setting of the large condenser (C_3). Then the large condenser was moved to the next division and readings were again taken on the Vernier condenser. The relationship between the Vernier readings and the readings on the

large condenser was obtained by taking two or three such sets of readings at each water-dioxane calibration mixture used. These data are given in Table VII and show that one division on the large condenser is equivalent to 31 divisions on the Vernier condenser. In order to convert the readings of the two condensers to one reading, assume the sixteenth division of the large condenser to be zero; then the seventeenth division will be 31, the eighteenth division will be 62, etc. The readings obtained in this way from the calibration solutions are also given in Table VIII.

The ten readings on the Vernier condenser for each solution varied by $\pm$ 0.3 division from the average value. Since this variation was in no definite order, it was concluded that there was no apparent gain or loss of water in the solution from the air while the measurements were being made. In order that no changes would occur due to differences in temperature, all of the readings on both the samples and the calibration mixtures were made at one time at a temperature of 21° C.

PURIFICATION OF WATER AND DIOXANE

All of the water that was used in this study was prepared in one batch. Distilled water was boiled for 30 minutes in a six-liter flask, the flask stoppered, and the water allowed to cool before use.

The dioxane was purified by refluxing it with sodium for 24 hours and then distilling it. The flask was then cleaned, fresh sodium added, the dioxane again refluxed for 24 hours, and again distilled.

TABLE VII

CALIBRATION OF DIELECTRIC RECEIVER WITH KNOWN WATER-DIOXANE MIXTURES

Water/50 cc. of Dioxane g.	Large Condenser Reading	Vernier Condenser Reading	Change in Vernier Reading*	Reading**
1.2065	16	51.0		51.0
1.1924	16	53.0		53.0
1.1924	15	84.3	31.3	
1.0005	18	29.5		91.5
1.0040	18	28.7		90.7
1.0040	17	59.3	30.6	
1.0040	16	90.8	31.5	
0.6894	20	26.2		150.2
0.6991	20	25.3		149.3
0.6991	19	56.1	30.8	
0.6991	18	87.0	30.9	
0.8341	19	31.2		124.2
0.8341	18	62.6	31.4	
0.8341	17	93.6	31.0	
0.5402	20	55.2		179.8
0.5084	20	61.5		185.5
0.5084	19	92.2	30.7	
0.3910	22	32.3		208.3
0.3771	22	36.0		212.0
0.3771	21	66.8	30.8	
		Av.	31.0	

* Difference in Vernier reading by change of one division on large condenser.

**Reading obtained by assuming the sixteenth division on large condenser to be zero and adding 31 for each number of the large condenser reading above 16 to the Vernier condenser reading.

PROCEDURE

The following procedure was approximately the same as that given by Freundjian and Jayne.

About four grams of pulp were placed in a pint fruit jar and covered with 400 cc. of the recently boiled and cooled distilled water. After the pulp had soaked for two hours, it was thoroughly disintegrated with a Lightnin mixer and further allowed to soak overnight. At the end of the soaking period, 200 cc. of the suspension were poured into a porous-glass filter funnel and sucked free of excess water. The pad so obtained was then quartered, and two portions were quickly transferred to tared weighing bottles and the other two portions to tared, stoppered 125 cc. Erlenmeyer flasks. The samples in the weighing bottles were dried to constant weight at 105° C.

The samples in the Erlenmeyer flasks were weighed, 50 cc. of purified dioxane added from a calibrated pipette, the flask tightly stoppered, and allowed to stand for 20 minutes with occasional shaking. At the end of this time the dioxane was filtered free of fibers through a 1-G-1 Jena crucible that had been dried in an oven at 105° C. for two hours and cooled in a desiccator over calcium chloride. The solution was then poured from the filter flask into an oven-dried bottle and the bottle tightly stoppered.

To avoid the possibility of error arising from a change in water content of the dioxane during filtration in the air, the calibration samples were prepared in a manner similar to the pulp samples--namely, by pipetting 50 cc. of the purified dioxane into a 125-cc.

Erlenmeyer flask. The flask was tightly stoppered and weighed. Then an approximate amount of the recently boiled and cooled distilled water was pipetted into the flask, and the flask again stoppered and weighed. The contents of the flask were then filtered through a dry 1-G-1 crucible, and the solution transferred from the filter flask to an oven-dried bottle.

RESULTS

The calibration data with known water-dioxane mixtures gave readings which all fell on a straight line. Samples with approximately the same amount of water gave readings that were approximately the same. It was rather surprising, then, that the data for the cellulosic materials did not check at all. These data are given in Table VIII. Examination of Table VIII shows that not only was there no trend in the amount of water bound by the various samples, but that the amount of water bound by two samples of the same material did not check. For example, one sample of the unacetylated material bound 6.58 per cent water and another sample bound 12.54 per cent water. This same irregularity was observed in all of the acetylated materials. Thus, samples of the material containing 2.06 per cent acetyl content bound 11.32 and 49.47 per cent water, whereas samples of the material containing 14.76 per cent acetyl content bound 8.64 and 0.14 per cent water.

In an attempt to explain why this method did not work on these materials, it is postulated that perhaps the water dissolved certain materials from the pulps that would affect the dielectric

TABLE VIII

RESULTS OF STUDY OF WATER BOUND BY ACETYLATED RAG STOCKS FROM LIQUID WATER

Acetyl Content of Sample %	Dielectric Reading	Wet Weight of Sample g.	Dry Weight of Sample g.	Water in Sample g.	Water in Dioxane g.	Water Bound by Sample g.	Water Bound %
0.00	99.3	1.5403	0.5467	0.9936	0.958	0.036	6.58
0.00	118.5	1.4380	0.5103	0.9277	0.862	0.064	12.54
1.24	84.0	1.5706	0.4641	1.1065	1.036	0.071	15.30
1.24	41.2	1.8407	0.5439	1.2968	1.260	0.037	6.83
2.08	24.2	1.9593	0.5478	1.4115	1.350	0.062	11.32
2.08	135.2	1.2506	0.3479	0.9009	0.728	0.172	49.47
3.11	104.1	1.2931	0.3246	0.9685	0.934	0.035	10.77
3.11	100.6	1.2940	0.3248	0.9692	0.950	0.019	5.85
4.42	99.2	1.5320	0.4239	1.1081	0.958	0.150	35.38
4.42	88.5	1.5245	0.4218	1.1027	1.086	0.017	4.03
5.31	201.3	0.8476	0.3880	0.4596	0.427	0.033	8.51
5.31	169.2	1.1267	0.5158	0.6109	0.596	0.015	2.91
6.85	92.9	1.5840	0.5595	1.0245	0.994	0.031	5.54
6.85	128.5	1.2918	0.4563	0.8355	0.806	0.030	6.57
8.16	150.6	1.1449	0.4209	0.7240	0.690	0.034	8.08
8.16	110.4	1.5247	0.5605	0.9640	0.950	0.014	2.50
10.36	190.9	1.3096	0.6337	0.6759	0.482	0.194	30.61
10.36	165.0	1.2050	0.5831	0.6219	0.616	0.006	1.03
14.76	122.4	1.3403	0.4628	0.8775	0.839	0.040	8.64
14.76	27.9	2.0487	0.7074	1.3413	1.332	0.001	0.14
18.24	97.5	1.5300	0.5607	0.9693	0.996	0.003	0.53
18.24	148.3	1.1349	0.4159	0.7190	0.702	0.017	4.09
22.92	167.5	1.3110	0.7094	0.6016	0.600	0.002	0.26
22.92	150.0	1.1753	0.6360	0.5393	0.538	0.001	0.16

constant. If different amounts of material were dissolved from different pulps, this would interfere with the determinations.

To check this possibility, the water in which the pulps of 3.11 and 22.92 per cent acetyl contents had been soaked, was added to dioxane and the dielectric readings of the resulting solutions were taken. These materials were chosen because if the water-binding properties followed the strength properties, the material of 3.11 per cent acetyl content should bind the most water of all the samples, and the material of 22.92 per cent acetyl content should bind the least.

The sample from the pulp with 3.11 per cent acetyl content had 0.9986 gram of water added to 50 cc. of dioxane, and gave a reading of 91.2. The sample from the pulp with 22.92 per cent acetyl content had 1.2043 grams of water in 50 cc. of dioxane and gave a reading of 52.6. Examination of the calibration data shows that both of these readings fall on the calibration curve, which seems to indicate that the erratic results mentioned above were obviously not due to substances dissolved in the water that had been in contact with the cellulosic materials.

There was also the possibility that the dioxane dissolved some material from the fibers that would change the readings. To check this possibility, 100 cc. of dioxane from the unacetylated sample were evaporated to dryness, but there was no residue; therefore, the erratic results obviously did not arise from this possible source of error.

Examination of the data of Table VIII also shows that an error could not have been produced from either of these causes. If the error had been due to material removed from the sample, it would vary according to the size of the sample. However, this was not the case. With the pulp of 3.11 per cent acetyl content, for example, the two samples were practically of the same size; yet one sample apparently bound 10.77 and the other only 5.85 per cent water.

Until further studies are made, no explanation can be offered for the failure of this method.

THE EFFECT OF ACETYLATION ON THE PAPERMAKING PROPERTIES OF MITSCHERLICH PULP

In order to determine if the same relation exists between the strength properties and the water-binding capacity of acetylated wood pulp as were found to exist for acetylated rag stock, a Mitscherlich pulp was acetylated to various degrees. Sufficient amounts of these materials were prepared to allow beating in the Lampén mill at intervals of 0, 5, 10, 20, and 40 minutes. A summary of the results of the strength evaluation of these runs is given in Table IX.

DISCUSSION OF STRENGTH PROPERTIES

The strength properties of the acetylated Mitscherlich pulps followed the same general trend as those of the acetylated rag stocks--that is, there was an initial increase in strength with the introduction of a small amount of acetyl content, but as the degree of acetylation increased, the strength properties fell rapidly until at 23 per cent acetyl content the materials had practically no strength.

TABLE IX A

SUMMARY OF STRENGTH RESULTS OF ACETYLATED MITSCHERLICH PULPS

Material	Unacetylated Mitscherlich pulp				
Beating Time, min.	0	5	10	20	40
Basis Weight	47.41	45.26	44.18	44.44	44.88
Caliper	4.63	3.45	3.19	3.08	3.03
Apparent Density	10.24	13.12	13.85	14.45	14.79
Burst Factor	32.7	118.2	145.3	155.5	153.7
Tensile Factor	11.09	38.95	43.52	47.59	41.91
Tear Factor	2.428	1.280	1.172	1.080	0.988

Material	2.61% acetyl content				
Beating Time	0	5	10	20	40
Basis Weight	47.78	48.69	47.22	46.83	46.42
Caliper	4.10	3.16	2.99	2.89	2.83
Apparent Density	11.65	15.41	15.79	16.20	16.40
Burst Factor	37.04	139.9	157.7	161.4	170.6
Tensile Factor	11.93	40.99	43.41	41.21	41.14
Tear Factor	2.746	1.203	1.118	1.140	0.979

Material	4.05% acetyl content				
Beating Time	0	5	10	20	40
Basis Weight	50.75	49.63	51.85	49.36	49.33
Caliper	4.06	3.29	3.23	3.07	2.98
Apparent Density	12.50	15.07	16.06	16.08	16.55
Burst Factor	41.8	149.3	161.2	163.3	167.0
Tensile Factor	11.33	40.54	44.67	43.76	43.10
Tear Factor	2.900	1.269	1.064	0.984	0.961

Material	6.75% acetyl content				
Beating Time	0	5	10	20	40
Basis Weight	48.72	59.54	51.71	48.48	49.81
Caliper	4.93	4.26	3.70	3.40	3.20
Apparent Density	9.88	13.97	13.97	14.26	15.56
Burst Factor	30.99	134.0	151.6	159.4	158.6
Tensile Factor	10.61	34.77	45.83	47.81	48.58
Tear Factor	2.463	1.183	1.009	1.095	1.020

Material	7.95% acetyl content				
Beating Time	0	5	10	20	40
Basis Weight	49.22	48.81	49.59	49.46	50.16
Caliper	5.23	3.64	3.51	3.38	3.41
Apparent Density	9.41	13.41	14.10	14.63	14.71
Burst Factor	21.8	127.8	140.5	146.6	149.3
Tensile Factor	8.25	35.03	39.32	39.58	47.66
Tear Factor	2.101	1.322	1.132	1.231	1.038

TABLE IX A (Cont.)

Material	12.98% acetyl content				
Beating Time	0	5	10	20	40
Basis Weight	49.99	49.21	45.46	49.66	44.51
Caliper	5.67	3.87	3.43	3.45	3.32
Apparent Density	8.81	12.72	13.25	14.10	13.41
Burst Factor	12.00	79.9	102.8	112.6	129.9
Tensile Factor	5.22	27.72	31.45	32.42	36.84
Tear Factor	1.216	1.418	1.126	1.031	1.020

Material	15.37% acetyl content				
Beating Time	0	5	10	20	40
Basis Weight	52.96	49.84	48.00	49.99	45.94
Caliper	6.44	4.16	3.78	3.68	3.13
Apparent Density	8.22	11.98	12.70	13.59	14.70
Burst Factor	11.3	43.5	56.8	66.0	81.2
Tensile Factor	4.15	18.78	21.84	25.52	25.99
Tear Factor	0.966	1.771	1.400	0.998	0.988

Material	18.97% acetyl content				
Beating Time	0	5	10	20	40
Basis Weight	61.29	65.14	63.27	47.89	73.20
Caliper	8.02	5.83	5.16	3.81	5.60
Apparent Density	7.64	11.17	12.26	12.56	13.06
Burst Factor	8.02	26.25	33.03	28.61	28.82
Tensile Factor	3.28	12.05	14.98	13.97	13.31
Tear Factor	0.796	1.721	1.598	1.015	0.742

Material	23.26% acetyl content				
Beating Time	0	5	10	20	40
Basis Weight	63.58	57.21	53.19	55.82	51.46
Caliper	9.63	6.51	5.53	5.75	5.13
Apparent Density	6.00	8.94	9.62	9.71	10.03
Burst Factor	0.00	5.06	4.10	4.46	5.62
Tear Factor	0.45	0.46	0.30	0.27	0.21

TABLE IX B

SUMMARY OF STRENGTH RESULTS OF ACETYLATED MITSCHERLICH PULPS
CALCULATED TO CELLULOSE BASIS

Material	Unacetylated Mitscherlich pulp				
Beating Time, min.	0	5	10	20	40
Drainage Time, sec.	3.9	4.5	5.6	9.9	15.9
Basis Weight	47.41	45.26	44.18	44.44	44.88
Caliper	4.63	3.45	3.19	3.08	3.03
Apparent Density	10.24	13.12	13.85	14.45	14.79
Burst Factor	32.7	118.2	145.3	155.5	155.7
Tensile Factor	11.09	38.95	43.52	47.59	41.91
Tear Factor	2.428	1.280	1.172	1.080	0.988

Material	2.61% acetyl content				
Beating Time	0	5	10	20	40
Drainage Time	3.9	4.7	6.7	14.1	28.3
Basis Weight	46.86	47.75	46.31	45.92	45.52
Caliper	4.10	3.16	2.99	2.89	2.83
Apparent Density	11.43	15.11	15.48	15.88	16.09
Burst Factor	37.8	142.6	161.1	165.7	173.9
Tensile Factor	12.16	41.80	44.26	42.03	41.95
Tear Factor	2.821	1.227	1.140	1.206	0.989

Material	4.05% acetyl content				
Beating Time	0	5	10	20	40
Drainage Time	4.3	5.4	7.0	12.7	43.2
Basis Weight	48.74	47.66	49.80	47.41	47.38
Caliper	4.06	3.29	3.23	3.07	2.98
Apparent Density	12.00	14.48	15.42	15.44	15.90
Burst Factor	43.5	155.5	167.1	170.0	173.9
Tensile Factor	11.80	42.21	46.50	45.56	44.87
Tear Factor	3.007	1.322	1.108	1.025	1.000

Material	6.75% acetyl content				
Beating Time	0	5	10	20	40
Drainage Time	4.4	4.5	8.2	19.2	97.0
Basis Weight	45.73	55.88	48.54	45.50	46.66
Caliper	4.93	4.26	3.70	3.40	3.20
Apparent Density	9.28	13.11	13.12	13.38	14.56
Burst Factor	33.0	142.8	161.5	169.0	169.3
Tensile Factor	11.33	36.14	48.83	50.94	51.69
Tear Factor	2.624	1.260	1.075	1.167	1.089

TABLE IX B (Cont.)

Material	7.95% acetyl content				
Beating Time	0	5	10	20	40
Drainage Time	4.9	6.4	12.2	36.5	137.0
Basis Weight	45.4	45.02	45.74	45.62	46.27
Caliper	5.23	3.64	3.51	3.38	3.41
Apparent Density	8.68	12.37	13.03	13.50	13.54
Burst Factor	23.8	138.6	152.5	158.9	161.9
Tensile Factor	8.94	37.98	40.44	42.93	51.67
Tear Factor	2.101	1.322	1.132	1.231	1.038

Material	12.98% acetyl content				
Beating Time	0	5	10	20	40
Drainage Time	4.6	5.2	7.5	33.7	236.9
Basis Weight	43.65	42.97	39.70	43.36	38.86
Caliper	5.67	3.87	3.43	3.45	3.32
Apparent Density	7.70	11.10	11.57	12.57	11.70
Burst Factor	13.7	91.3	117.8	128.9	148.6
Tensile Factor	5.60	31.74	36.03	37.13	42.20
Tear Factor	1.395	1.624	1.290	1.188	1.168

Material	15.37% acetyl content				
Beating Time	0	5	10	20	40
Drainage Time	4.3	4.7	6.2	14.3	94.7
Basis Weight	45.02	42.36	40.76	42.49	39.05
Caliper	6.44	4.16	3.78	3.68	3.13
Apparent Density	7.00	10.13	10.78	11.55	12.47
Burst Factor	13.3	51.2	66.7	77.7	95.8
Tensile Factor	4.89	22.12	22.00	30.03	30.57
Tear Factor	1.137	2.084	1.648	1.174	1.165

Material	18.97% acetyl content				
Beating Time	0	5	10	20	40
Drainage Time	3.5	3.5	4.0	8.6	26.8
Basis Weight	50.23	53.39	51.86	39.25	59.99
Caliper	8.02	5.83	5.16	3.81	5.6
Apparent Density	6.26	9.16	10.05	10.30	10.71
Burst Factor	9.8	32.0	40.3	34.9	35.2
Tensile Factor	4.00	14.73	18.28	17.07	16.23
Tear Factor	0.971	2.109	1.949	1.238	0.907

Material	23.26% acetyl content				
Beating Time	0	5	10	20	40
Drainage Time	4.1	4.9	5.7	5.5	7.1
Basis Weight	49.13	44.21	41.11	43.1	39.77
Caliper	9.63	6.51	5.53	5.75	5.13
Apparent Density	5.10	6.79	7.43	7.40	7.75
Burst Factor	0.0	6.56	5.33	5.77	7.27
Tear Factor	0.586	0.706	0.389	0.345	0.269

On the other hand, the increase in the strength properties with the introduction of very small amounts of acetyl was not nearly so great in the case of the acetylated Mitscherlich pulps as it was in that of the acetylated rag stocks. Nevertheless, there was a definite increase in the case of the Mitscherlich pulp.

Within a range of acetyl content of from 2.5 to 6.75 per cent the bursting strength increased about ten per cent over the unacetylated pulp. The sample with 7.95 per cent acetyl content had a slightly higher bursting strength than did the unacetylated material, but with the introduction of more acetyl, the bursting strength fell rapidly. The material with an acetyl content of 23.26 per cent had zero bursting strength in the unbeaten condition and developed a maximum value of only 7.27 points per 100 pounds as compared with a maximum value of 155.5 points per 100 pounds for the unacetylated material.

The results for tensile strength were somewhat more variable than those for bursting strength, but the material with 6.75 per cent acetyl content showed an increase in tensile strength of about eight per cent over the unacetylated material. With the introduction of more acetyl into the pulp, the tensile strength dropped below that of the unacetylated pulp. The tensile strength of the material with 18.47 per cent acetyl content was about one-third that of the unacetylated pulp.

There was little difference in the tearing strengths of the beaten materials at the various degrees of acetylation until an acetyl content of 23.26 per cent had been reached, when the tearing strength

was about only one-third that of the unacetylated pulp. The unbeaten sheets, however, showed, at an acetyl content of 4.05 per cent, an increase in tearing strength of about 25 per cent over the unacetylated pulp. With the materials containing more than 13 per cent acetyl, the tearing strengths of the unbeaten materials were lower than the values at the five-minute beating interval. This same abnormal effect has been observed by the Institute pulping department on very hard kraft stocks that were difficult to beat; this effect is probably due to incomplete defiberation of the materials at the zero interval.

The increases in strength of the acetylated Mitscherlich pulps at low degrees of acetylation, although small, may be explained in the same way as those for the acetylated rag stock at low degrees of acetylation. That is, a small percentage of acetyl content may be expected to open up the internal structure of the fiber so that more hydroxyl groups are available for hydration and subsequently for fiber-to-fiber bonding, although a few of the hydroxyl groups have been covered up.

To explain why, within the range of low acetyl contents, smaller increases in strength were obtained with the acetylated Mitscherlich pulps than with the acetylated rag stocks, the assumption may be made that some of the pentosans present in the pulp were acetylated but dissolved in the acetylation mixture and thus removed on washing. Hence, there would be a loss in strength due to removal of pentosans, and this loss could partly offset the increase in strength due to the opening up of the internal fiber structure. To test this assumption, pentosan determinations were made on the acetylated Mitscherlich pulps

(according to the Institute method), with the following results:

Acetyl Content %	Pentosan Content %
0.00	5.7
2.61	5.0
4.05	5.0
6.75	4.1
7.95	5.3
12.98	4.5
15.37	4.2
18.47	4.1
23.26	3.9

It is seen that as the acetyl content of the materials increased, the pentosan content (calculated on the acetyl-free basis) steadily decreased, with the exception of the material with 7.95 per cent acetyl, which had a higher pentosan content than any of the other acetylated materials. Reference to Table III shows that the material with 7.95 per cent acetyl was prepared in a shorter time than any of the other acetylated materials, and this probably accounts for the fact that a smaller amount of pentosan was dissolved out of this sample. The material with an acetyl content of 7.95 per cent had strength properties almost the same as those of the unacetylated material. In the acetylated rag stocks the material with 8.36 per cent acetyl had strength properties about the same as those of the unacetylated material.

Although there is no doubt that pentosans have been removed on acetylation, it is difficult to say whether the small amounts actually removed can account for the fact that the partial acetylation up to a certain limit increased the strength properties to a smaller extent than in the case of the rag stocks.

The results obtained with both types of cellulosic material may be summarized as follows: In both rag stock and Mitscherlich pulp, the introduction of acetyl content up to eight per cent caused an increase in strength properties, assumed to be due to the opening up of the internal fiber structure. In the case of the Mitscherlich pulp, however, this effect was less pronounced and it is possible that it was partially offset by the removal of pentosans from the pulp during the acetylation procedure. In both materials an acetyl content above eight per cent caused the strength properties to fall to values much lower than those of the unacetylated materials.

DISCUSSION OF DRAINAGE TIME

The acetylated Mitscherlich pulps, as well as the acetylated rag stocks, show no correlation between drainage time and strength properties. The maximum strength values of the acetylated Mitscherlich pulps were obtained in the range of 4-7 per cent acetyl content, but the maximum drainage time was at 12.98 per cent acetyl content. In the materials having an acetyl content above 12.98 per cent, the drainage time decreased. At an acetyl content of 23.26 per cent the material had practically lost its ability to develop slowness, for there was only a three-second increase in drainage time over the entire beating period as compared with a nineteen-second increase for the unacetylated material.

DISCUSSION OF APPARENT DENSITY

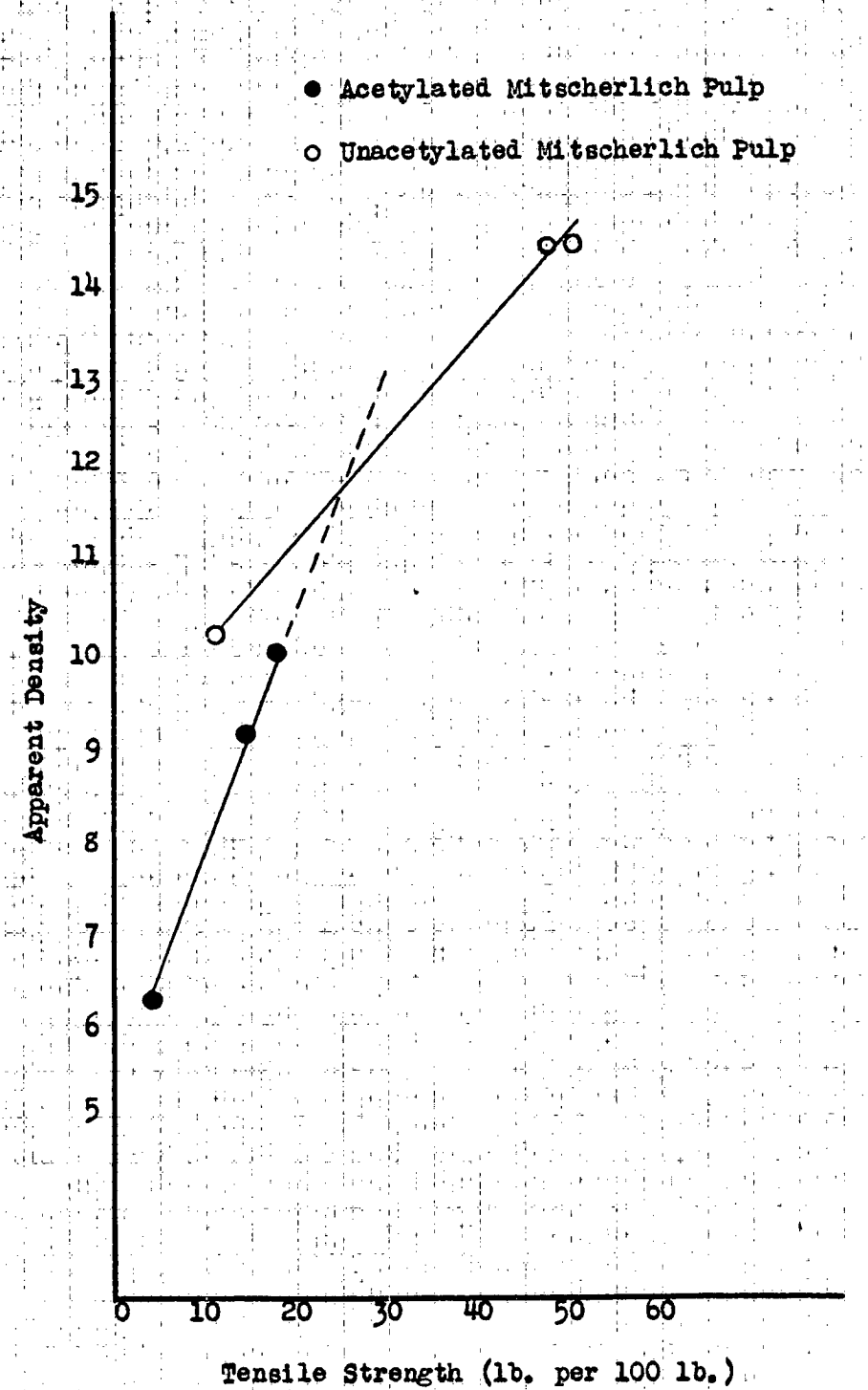
Doughty (7) found that, as the solid fraction of a sheet was increased either by beating or pressing, there was a straight line correlation between the solid fraction and tensile strength. In Figure 4 the tensile strengths of the unacetylated Mitscherlich pulp and of the material with 18.47 per cent acetyl content are plotted against their apparent densities. In each of these materials, up to the development of maximum strength, there was an approximate straight line relationship between tensile strength and apparent density. Examination of the slopes of the curves, however, shows that in the case of the acetylated material the slope of the curve was much greater than that of the unacetylated material. This indicates that for any given change in apparent density, the acetylated pulp would have a smaller increase in strength than the unacetylated pulp. The acetylated pulp, then, would have to have more fiber-to-fiber contacts than the unacetylated pulp in order to have the same strength; therefore, the covering up of the hydroxyl groups by acetyl groups decreased the bonding force per unit fiber-to-fiber contact.

DISCUSSION OF RATE OF DEVELOPMENT OF STRENGTH PROPERTIES

The rate of development of strength properties was approximately the same on all of the acetylated Mitscherlich pulps. In nearly all of the samples the maximum strength values were reached after 20 minutes of beating, and remained fairly constant up to the 40-minute beating interval. Any beating interval between 20 and 40 minutes could have been used on this material and a representative

FIGURE 4

TENSILE STRENGTH-APPARENT DENSITY RELATIONSHIP
OF ACETYLATED AND UNACETYLATED MITSCHERLICH PULP



picture of the strength properties would have been obtained from the one beating interval. Therefore, it is likely that the strength values obtained at the one beating interval on the rag stock were also representative.

RESULTS OF HYGROSCOPIC STUDY (Method 1) ON ACETYLATED MITSCHERLICH PULPS

A hygroscopic study was made on the acetylated Mitscherlich pulps using the same apparatus and procedure as was used for the acetylated rag stocks. In the case of the acetylated Mitscherlich pulps, however, measurements were made at only one relative humidity (91.2 per cent) with the following results:

Acetyl Content of Material %	Water Bound by Material %
0.00	15.10
2.61	15.02
4.05	15.16
6.75	14.39
7.95	13.55
12.98	11.98
15.07	10.79
16.97	10.08

The results of the hygroscopic study on the acetylated Mitscherlich pulps correlates fairly well with their strength properties. The small increase in strength properties of these materials was in the range of 2.61 to 7.95 per cent acetyl content. Beyond 7.95 per cent acetyl content, the strength properties of the materials dropped off rapidly with the introduction of more acetyl group. The water-binding properties of the materials of acetyl content from zero to 4.05 per cent were practically the same; beyond the latter value,

the amount of bound water dropped with increasing acetyl content. The material containing 18.97 per cent acetyl content bound 10.08 per cent water as compared with 15.10 per cent for the unacetylated material.

EFFECT OF PENTOSANS UPON THE BONDING STRENGTH OF PAPER

After the role which the hydroxyl groups in cellulose play in the water-binding and -bonding reactions had been established and reaffirmed, the assumption could be made that the beneficial effect which the presence of pentosans exerts upon the strength properties of a sheet of paper may be due to a similar mechanism. In other words, the effect of the pentosans may presumably be likewise a function of their hydroxyl groups.

Thus, it could be hoped to arrive at a positive conclusion by applying the same technique that has proven so helpful in the pure cellulose-water system. Accordingly, the addition of acetylated pentosans--i.e., those in which free hydroxyl groups are no longer available--to cellulose fibers should fail to produce any increase in the strength properties of a sheet prepared from a beaten mixture of the two components.

Various possibilities suggest themselves to explain how the hydroxyl groups of pentosans in a cellulose-pentosan-water system may become active and contribute to the bonding effect. These possibilities are discussed later in this section.

EXPERIMENTAL PROCEDURES FOR STUDIES ON THE EFFECT OF ADDING PENTOSAN TO RAG STOCK IN THE BEATER

RAW MATERIAL

The pulp used for the study of the effect of pentosans on the bonding strength of paper was the same rag stock used in the earlier acetylation studies. This material was practically pure cellulose (with an alpha-cellulose content of 98.15 per cent) and contained no pentosans. Xylan (which had been used by Jonas and Reith (19) and by Obermanns (20)) was chosen as a typical representative of the pentosans.

About a pound of impure xylan was obtained for this investigation from the material prepared by Institute students from wheat straw by the method of Salkowski (30), as modified by Heuser and Braden (31). This material, which had not been purified, had an ash content of 8.06 per cent; the ash was high in copper, because of the use of copper sulfate as a means of precipitation.

PURIFICATION OF XYLAN

In order to reduce the ash content and brighten the rather dark color of the xylan, it was purified by the following procedure. The crude xylan was triturated with 1500 cc. of hydrochloric acid (d. 1.12 diluted with an equal volume of water), filtered with suction on a Büchner funnel, and the filtrate discarded. The residue was then triturated with 95 per cent ethyl alcohol to a thin slurry, the slurry poured into ten gallons of alcohol, and the xylan allowed to settle for 24 hours; the alcohol was siphoned off, the xylan thickened

by filtration, and spread out on clay plates to dry. When dry, the xylan was ground in a mortar, and the trituration with acid, washing with alcohol, drying, and grinding were repeated. The two acid treatments removed most of the ash content of the xylan, but it still had the dark color of the crude xylan.

In an attempt to remove the color, the ground xylan was triturated with eight liters of water, chlorine gas was passed into the slurry with stirring for several minutes, and the xylan allowed to remain in contact with the chlorine water for 24 hours; the chlorinated material had a very dark brown color. To remove the chlorinated products, the material was dissolved in ten liters of two per cent sodium hydroxide, and the xylan was precipitated by pouring it into ten gallons of alcohol; after the xylan had been allowed to settle overnight, the alcohol was siphoned off, five gallons of fresh alcohol were mixed with the xylan, and the xylan again allowed to settle. When it had settled, and after the alcohol had been siphoned off, the filtered xylan was dried on clay plates. This material had a lighter color than the crude xylan.

To remove the remainder of the coloring matter from the xylan, the precipitated material was dissolved in eight liters of two per cent sodium hydroxide; concentrated hydrochloric acid was added to give a neutral solution, which precipitated the xylan as a finely divided material. In accordance with the method of purification applied by Ernest Anderson to a number of hemicellulose preparations, this suspension was brominated for an hour by the addition of liquid bromine and then poured into ten gallons of alcohol to remove the

bromine and the brominated products. After the xylan had been allowed to settle for 24 hours, the alcohol was siphoned off, five gallons of fresh alcohol were mixed with the xylan, and the xylan again allowed to settle for 24 hours. At the end of this time, the alcohol was siphoned off, the xylan--which was now very white in color--was filtered and spread out on clay plates to dry. Upon drying, the color changed to a grayish white.

Undoubtedly the xylan suffered some degradation during this purification procedure. To remove any fractions soluble in water the material was triturated with five liters of softened water, the slurry poured into five gallons of softened water, and the xylan allowed to settle overnight. The water was then siphoned off and four gallons of fresh softened water were mixed with the material. When the xylan had settled, the water was removed by siphoning. As the aqueous suspension was rather difficult to filter, four gallons of 95 per cent alcohol were mixed with the wet residue, the mixture allowed to stand for 24 hours, the alcohol was siphoned off, and the xylan thickened by filtration. To remove any remaining water, the material was washed by mixing it with ten liters of 95 per cent alcohol, filtering, mixing with three liters of absolute alcohol, and again filtering. The alcohol was removed from the xylan by mixing it twice with two-liter portions of ether. The filtered material was spread out on clay plates to dry, ground in a mortar, and stored in a sealed jar. The purified material still had a grayish-white color.

The ash, moisture, and pentosan content of the purified xylan were determined according to Institute Methods.

Moisture	21.85%
Ash	0.659%
Pentosans	85.6%

The ash was white and did not give a test for copper. The pentosan content indicates that the material was not pure; however, the constant for converting the amount of furfural produced by boiling with 12 per cent hydrochloric acid was obtained from xylose, and it may not apply strictly to pentosans. At any rate, this material was considered satisfactory for the following investigation.

ACETYLATION OF XYLAN

The acetylated xylan was prepared by the method of Heuser and Schlosser (32), in which the xylan was heated for one hour at 70° C. with a mixture of 4.0 cc. of acetic anhydride and 35 cc. of pyridine per gram of xylan.

Forty grams of xylan were acetylated by this method. Upon acetylation the xylan dissolved to give a light brown solution, but when the solution was allowed to stand for 30 minutes, a dark brown jelly settled to the bottom. This jelly had also been observed by Heuser and Schlosser and had been discarded.

In the present study, the clear, supernatant liquid was poured into five gallons of 95 per cent alcohol to precipitate the acetylated xylan and to remove the acetylation mixture. After the acetylated xylan had settled, the alcohol was siphoned off, and the acetylated material was washed twice by mixing with two-gallon portions of alcohol and siphoning off the alcohol. The acetylated xylan was thickened on a hard filter paper, and the alcohol was removed by

washing twice with one-liter portions of ether. The material, still wet with ether, was transferred to a vacuum desiccator and dried over calcium chloride. After drying, the acetylated xylan was rather hard and lumpy and was ground to a light tan powder. The yield was 23.6 grams. This material was designated as acetylated xylan I.

As a matter of interest, the brown jelly material that settled from the solution was precipitated in alcohol, washed, and dried in the same manner as the soluble acetylated xylan. Upon drying, this material formed a very fine tan powder. The color was lighter than that of acetylated xylan I. The yield was 26.3 grams. This material was designated as acetylated xylan II.

The pentosan content of the acetylated xylan was determined by Institute Tentative Method 424A, and the acetyl content was determined by the method used for cellulose acetate. The moisture contents of the materials were also determined.

Material	Acetylated Xylan I	Acetylated Xylan II
Moisture, %	2.0	2.2
Pentosan, %	(92.3)* 55.9	(82.7)* 50.3
Acetyl, %	39.37**	39.10**

* The pentosan content calculated on the acetyl-free basis.

**Theoretically xylan diacetate contains 39.82 per cent acetyl.

The pentosan and acetyl contents show that the insoluble jelly material was also an acetylated xylan; however, the pentosan content of acetylated xylan I is somewhat higher than that of acetylated

xylan II.

METHOD OF BEATING AND TESTING

The pulps were beaten in the Lampén mill and sheets were made and tested by the same methods used in beating and testing the acetylated rag stocks. An eighteen-gram charge of rag stock was used in the Lampén mill.

ADDITION OF XYLAN TO THE BEATER

In order to determine the effect of soaking the xylan before beating on the strength properties of the pulp beaten with the xylan, four samples of rag stock, to which five per cent of xylan (on the weight of the rag stock) had been added, were beaten for 30 minutes in the Lampén mill. Before beating, the rag stock and xylan were pretreated in the following manners.

(A) The rag stock and xylan were soaked together overnight, defibered together, and beaten together.

(B) The rag stock and xylan were soaked separately overnight, the rag stock was disintegrated, and the xylan added to the rag stock in the Lampén mill.

(C) The rag stock was soaked overnight and disintegrated. Dry xylan was added to the rag stock in the Lampén mill.

(D) The rag stock was soaked overnight, and dry xylan was added in the Lampén mill.

The strength properties of the sheets made from these materials are given below.

Sample	A	B	C	D	Unacetylated Rag Stock
Drainage Time	15.8	18.0	18.1	17.7	
Basis Weight	50.22	51.27	49.44	46.86	43.2
Caliper	4.29	4.23	4.08	3.96	4.7
Apparent Density	11.71	12.16	12.13	11.83	9.2
Burst Factor	70.3	70.1	69.9	69.4	62.8
Tensile Factor	22.5	23.2	23.3	22.6	18.45
Tear Factor	2.995	2.283	3.095	2.913	3.70

These figures show that it makes little difference how the xylan is incorporated into the pulp. Therefore, the simplest way was shown--namely, the addition of the dry xylan directly to the stock in the Lampén mill.

Obermanns (20) found that when xylan was added to rag stock in the beater, the amount of xylan retained in the sheet increased with the degree of beating. He selected the pentosan content of the sheets prepared from materials of 500 cc. S. R. freeness as a representative value for the amount of pentosan retained in the sheets. His results showed that, when the material had a pentosan content of 3.63 per cent at 500 cc. freeness, the tensile, tearing, and folding strengths of the material were appreciably higher than those of the rag stock to which no pentosan had been added. When larger amounts of xylan were added to the rag stock, the tensile strength continued to increase, but the bursting and tearing strengths decreased. When the material contained 6.48 per cent pentosan at 500 cc. freeness, the increase in tensile strength over that of the material to which no pentosan had been added was about twice as large as the increase when the material contained 3.63 per cent pentosan. This showed that the

increase in tensile strength was approximately linear with the amount of pentosan retained by the sheet. At a pentosan content of 6.48 per cent, however, the tearing strength of the sheet had fallen to a value just above that of the material with no added pentosan, and the folding strength had fallen to a value below that of the untreated material.

In this study, four series of beater runs were made with beating intervals of 5, 10, 20, 40, and 60 minutes. In the first series of runs, rag stock was beaten with no addition of xylan. In one series of runs xylan equal to five per cent of the weight of the rag stock and in another series ten per cent of xylan were added to the rag stock in the Lampén mill at each interval. In the fourth series of runs, acetylated xylan II equivalent to ten per cent of xylan (or about 20 per cent of acetylated xylan) was added.

DISCUSSION OF RESULTS OF ADDITION OF XYLAN TO RAG STOCK IN THE BEATER

PENTOSAN RETAINED IN THE SHEET

The pentosan contents of the sheets from the materials beaten with xylan and acetylated xylan were determined according to Institute Tentative Method 424A; the results are given in Table X. The figures represent the amounts of the added material actually retained by the sheet. Since the pentosan content of the xylan was 85.6 per cent, the pentosan contents of the materials were divided by 0.856 to give the actual xylan content retained by the sheet. The acetylated xylan content of the sheets to which acetylated xylan had been added was determined in a similar manner. The acetylated xylan

contents were also calculated to an acetyl-free basis.

The results confirm the findings of Obermanne--namely, that the longer the xylan and cellulose are beaten together, the more xylan is retained when the material is made into a sheet. The acetylated xylan also shows this behavior.

DISCUSSION OF STRENGTH DATA

The strength data of this study are given in Table XI and Figures 5, 6, and 7. The addition of five per cent xylan to rag stock in the beater caused an appreciable increase in the bursting and tensile strengths of the sheets made from the material, and the addition of ten per cent xylan caused an additional increase. On the other hand, the addition of acetylated xylan to the rag stock in the beater caused an appreciable decrease in both bursting and tensile strengths.

As regards the tearing strength, this property was slightly decreased by the addition of xylan and slightly further decreased by the addition of acetylated xylan (ten per cent added in both cases).

The addition of xylan to the rag stock in the beater increased the apparent density of the sheets made from the materials, but the addition of acetylated xylan had little effect (Figure 6).

As stated earlier, several investigators have found that, with increasing pentosan content, the drainage time is greatly increased. The results of this investigation (Table XIA) confirm this fact. However, when acetylated xylan was added to the rag stock, the drainage time had the tendency to approach the values of the rag stock

TABLE X

XYLAN RETAINED IN SHEETS UPON BEATING

Five Per Cent Xylan Added to the Beater

Beating Time Min.	Xylan Retained %
5	1.9
10	1.9
20	2.4
40	2.7
60	2.9

Ten Per Cent Xylan Added to the Beater

Beating Time Min.	Xylan Retained %
5	2.4
10	3.0
20	3.2
40	3.3
60	3.4

Ten Per Cent Acetylated Xylan (on Acetyl-Free Basis) Added to Beater

Beating Time Min.	Acetylated Xylan Retained %	Retention on Basis of Xylan %
5	4.0	2.4
10	3.9	2.4
20	4.0	2.4
40	5.6	3.4
60	7.1	4.3

TABLE XIA

EFFECT OF ADDED XYLAN AND ACETYLATED XYLAN ON THE STRENGTH PROPERTIES OF RAG STOCK

Rag Stock Alone

Beating Time	5	10	20	40	60
Drainage Time	8.1	9.1	10.9	19.6	22.5
Basis Weight	45.16	45.38	49.58	48.01	48.42
Caliper	5.44	4.87	4.94	4.45	4.35
Apparent Density	8.30	9.32	10.03	10.79	11.13
Burst Factor	56.25	71.18	65.35	60.19	56.59
Tensile Factor	15.72	19.52	20.71	20.60	19.95
Tear Factor	5.839	4.625	3.705	2.626	2.247

Five Per Cent Xylan Added

Beating Time	5	10	20	40	60
Drainage Time	7.7	9.3	14.0	20.1	44.5
Basis Weight	42.9	50.8	50.6	48.3	52.7
Caliper	5.53	5.61	5.06	4.45	4.46
Apparent Density	7.75	9.05	9.99	10.85	11.81
Burst Factor	55.05	71.53	70.21	65.90	58.43
Tensile Factor	14.18	19.72	23.75	22.45	21.33
Tear Factor	4.579	4.640	3.877	2.535	1.955

Ten Per Cent Xylan Added

Beating Time	5	10	20	40	60
Drainage Time	7.8	10.4	19.2	36.0	88.9
Basis Weight	50.38	49.64	50.98	51.38	52.87
Caliper	6.33	5.41	5.09	4.62	4.38
Apparent Density	7.96	9.18	10.01	11.12	12.08
Burst Factor	63.32	77.56	78.07	67.34	61.47
Tensile Factor	14.59	21.90	23.44	23.61	23.11
Tear Factor	5.486	4.146	3.582	2.528	1.912

Ten Per Cent Acetylated Xylan (on Basis of Xylan) Added

Beating Time	5	10	20	40	60
Drainage Time	9.6	9.6	12.0	15.7	38.4
Basis Weight	46.18	44.59	47.71	46.54	49.62
Caliper	5.24	4.76	4.81	4.40	4.24
Apparent Density	8.76	9.37	9.92	10.58	11.70
Burst Factor	60.63	63.46	55.54	50.49	36.70
Tensile Factor	16.28	18.15	19.60	14.31	15.12
Tear Factor	3.869	4.023	3.246	2.407	1.342

TABLE XIB

EFFECT OF ADDED XYLAN ON ACETYLATED RAG STOCK (22.92 % Acetyl Content)

Beating Time 45 Minutes

Material	Acetylated Rag Stock	11.4 % Xylan added to acetylated rag stock
Drainage Time	5.1	5.3
Basis Weight	60.33	57.11
Caliper	9.20	8.26
Apparent Density	6.45	6.94
Burst Factor	4.97	4.34
Tensile Factor	4.39	3.94
Tear Factor	0.354	0.280

alone, as could have been expected.

These results confirm the observations of other investigators and show that the addition of xylan to stock in the beater increases the bonding strength of the sheet made from the beaten material. In addition, they show that xylan whose hydroxyl groups have been covered by acetyl groups do not increase the bonding strength of the sheet, but rather decrease it. Thus, it is obvious that the beneficial effect of xylan, and very likely of other pentosans, upon the bonding strength within a sheet of paper is a function of its free hydroxyl groups. Acetylated xylan with free hydroxyl groups no longer available may be considered to act merely as a filler between the pulp fibers.

FIGURE 5

EFFECT OF ADDED XYLAN ON STRENGTH PROPERTIES OF RAG STOCK

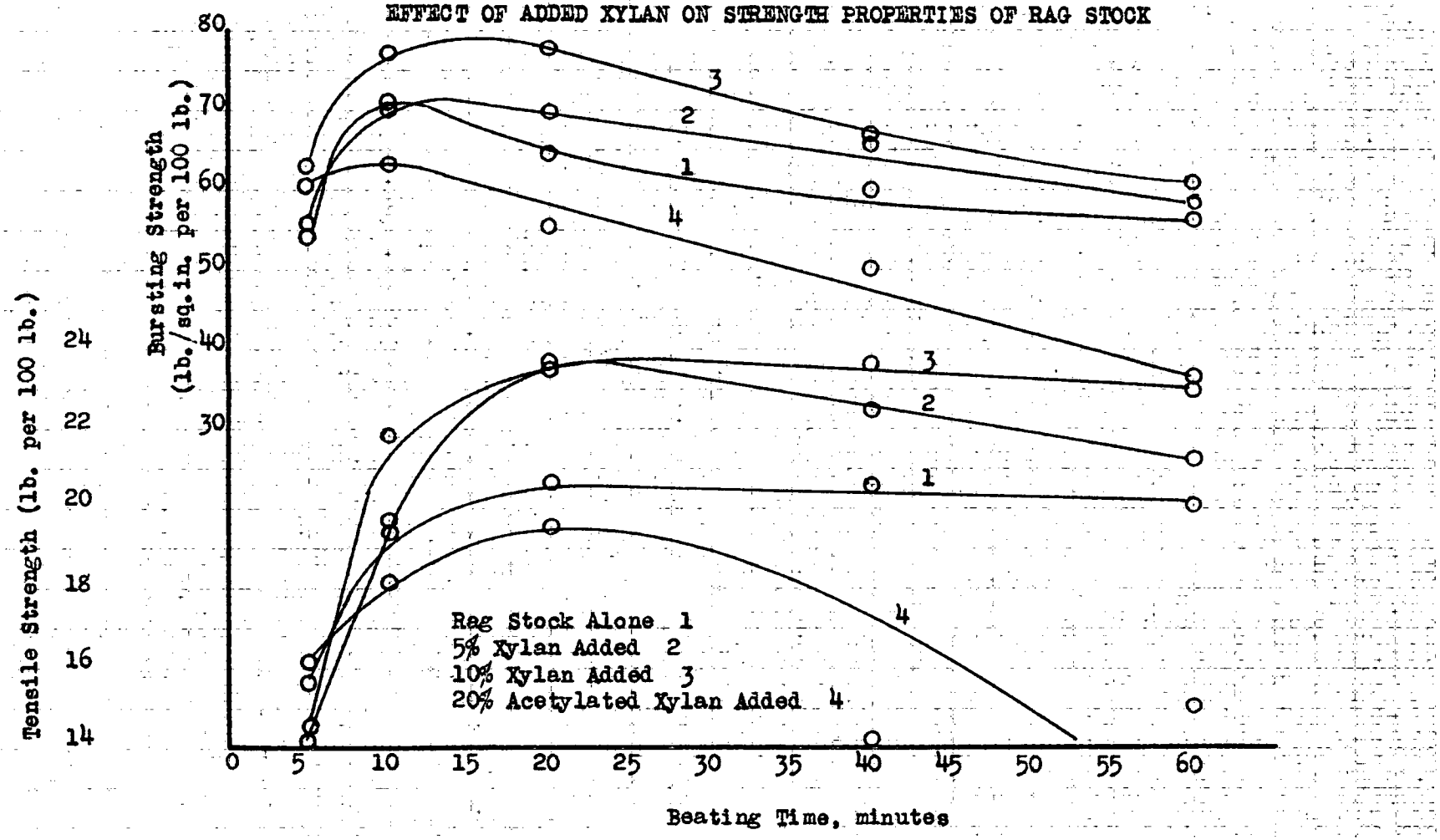
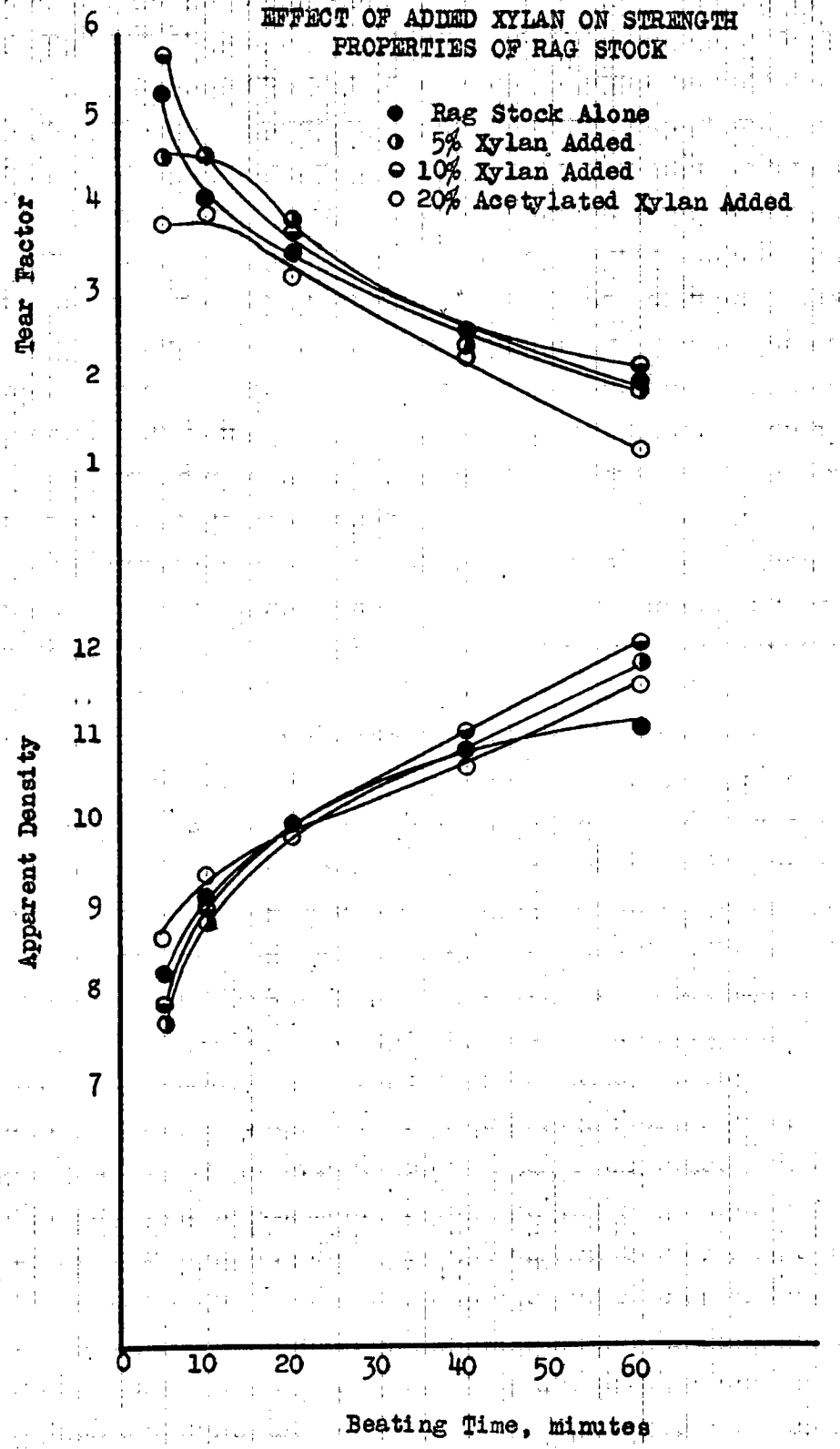


FIGURE 6

EFFECT OF ADDED XYLAN ON STRENGTH PROPERTIES OF RAG STOCK



BEATING OF ACETYLATED RAG STOCK TO WHICH XYLAN HAD BEEN ADDED

The question then arose as to the function of the hydroxyl groups of the xylan.

In the case the pentosan is a constituent of the cellulose fiber--i.e., deposited within the fiber cell walls, its beneficial effect upon the strength properties of a sheet of paper made from such material has been explained by Rowland and Young (15) on the assumption that, because of its ability to become more easily hydrated than the cellulose fiber, an osmotic effect occurs--i.e., water is drawn from the outside through the fiber membrane into the interior of the fiber and thus increases the swelling of the fiber. Consequently, the more highly swollen fibers are more easily hydrated, with a resulting increase in bonding when the sheet is formed and the water is removed.

If it were possible to acetylate xylan as it is deposited within the fiber cell walls without simultaneously acetylating the cellulose constituent, it is likely that the osmotic effect would be inhibited and no increase in swelling and bonding of such fibers would result.

However, in the present experiment xylan was added to the fiber and thus only a mechanical mixture was produced. In this case, osmotic effects must be expected to be limited, and the addition of xylan would merely lead to an increase in the system of the free hydroxyl groups with subsequent increased opportunity for hydration and bonding.

On the other hand, the assumption may be made that the function of the hydroxyl groups of the xylan is to combine with the hydroxyl groups of the cellulose in much the same way that, in a pure cellulose-water system, water molecules are attached to the free hydroxyl groups in a first phase of the mechanism. But, as the water is recovered and the surfaces of the fibers (which contain xylan between them) are drawn together more closely, the secondary valences of the free hydroxyl groups of the cellulose and those of the xylan become operative, resulting in mutual attraction and bonding. The xylan would thus act as a cementing material between individual cellulose fibers which would explain the increased strength properties of the sheet.

It was thought that a decision between the two explanations could possibly be used by adding unacetylated xylan to acetylated fibers which had practically lost their papermaking properties.

If the effect of the xylan were due merely to an increase in the number of free hydroxyl groups in the system, one could expect that an addition of xylan to such acetylated fibers would result in increased hydration of the mixture and subsequent increased bonding—i.e., increased strength of the sheet. If, on the other hand, no such increase occurred, the result would be in favor of the second explanation, according to which free hydroxyl groups must be accessible in the fiber so that they may combine with the hydroxyl groups of the xylan.

It may be calculated that acetylated rag stock with 22.92 per cent acetyl content had 37.09 per cent of the hydroxyl groups

available in the cellulose covered by acetyl groups. It appears fairly safe to assume that the greater part of these acetyl groups are located on the surfaces of the micelles. Mark and Meyer (33) have calculated that about 30 to 50 per cent of the hydroxyl groups in cellulose are exposed on these surfaces. The fact that the rag stock with 22.92 per cent acetyl content had practically no bonding strength would make it seem probable that the bonding strength in a sheet of paper made of cellulose fibers arises from about one-third of the hydroxyl groups. In other words, the remainder of the hydroxyl groups are locked in the interior of the micellar structure and are not accessible to water, and thus are not involved in the bonding reaction, unless they are made accessible by the application of special means.

If the strength-improving effect of pentosans is the result of a bonding between its hydroxyl groups and those of cellulose, such bonding can be expected to occur only if the cellulose supplies the necessary number of free hydroxyl groups. In rag stock acetylated to the extent of 37.09 per cent of all available hydroxyl groups, no such free hydroxyl groups should be accessible, and, if the second explanation is correct, the addition of unacetylated xylan to such acetylated rag stock should exert no strength-increasing effect.

The following experiment was carried out. Twenty-four grams of acetylated rag stock (having an acetyl content of 22.92 per cent) and 11.2 per cent xylan (on the basis of the acetyl-free pulp) were beaten in the Lampén mill for 45 minutes. The strength properties of the sheets made from these materials and of the rag

stock beaten without the addition of xylan are given in Table XIB.

It is seen that the beating of the acetylated rag stock in the presence of xylan did not result in an increase of the strength properties, but rather produced a slight decrease. This result may then be explained by the lack of accessible hydroxyl groups in the acetylated rag stock. The slight decrease of the strength properties seems to indicate that the xylan acted as a filler and thus has still further reduced any opportunity for hydration and bonding.

PROCESSING IN ACETONE

Bletzinger has shown that when acetylated fibers, which are not wetted and swollen by water, are beaten in a medium, such as acetone, which wets and swells the acetylated fiber without dissolving it, a sheet of great strength (even greater than that of the unacetylated material beaten in water) is obtained.

Bletzinger also found fibrous cellulose acetate with 25 per cent acetyl content need only to be stirred in the British disintegrator to defiber the clumps thoroughly and to give a suspension in which the refractive index of the fibers appeared to be almost the same as that of the acetone.

The sheets made from the acetylated rag stock thus disintegrated in acetone had a bursting strength of 139 lb./sq.in. per 100 pounds basis weight, whereas the best strength developed on beating rag stock in water was 56 lb./sq.in. The tensile strength of the acetate was 31.4 pounds per 100 pounds basis weight, but that of

the rag stock was only 18.7 pounds. The tear factors and apparent densities were about the same in both cases. These results indicated that, for the same number of fiber-to-fiber contacts, the bonding forces between the acetylated fibers defibered in acetone were much greater than those between the unacetylated fibers beaten in water. This result was found to be in agreement with the interesting observation that the sheets of paper prepared from the acetylated fiber in acetone showed a high resistance to water and were entirely inkproof.

In addition, Bletzinger observed that, although unacetylated rag stock was apparently wet by acetone, it could not be defibered in the British disintegrator. Acetylated fibers of 8.12 per cent acetyl content, however, could be disintegrated in acetone and formed into sheets. These sheets, however, had strength properties much less than those of the same acetate beaten in water and those of unacetylated rag stock beaten in water. Beating the 8.12 per cent acetyl content material in acetone appreciably increased its strength properties, but these were still only about half that of the same material beaten in water.

Pressing increased the apparent density of the processed cellulose acetates but did not increase their strength properties.

To check the results of Bletzinger and to determine the behavior of a material with a high acetyl content upon being processed in the beater, an acetylated rag stock of 23.49 per cent acetyl content and an acetylated Mitscherlich pulp of 23.26 per cent acetyl content were processed in acetone in the Lampén mill.

BEATING PROCEDURE

Samples corresponding to 15 grams of dry (calculated to acetyl-free) material of the acetylated Mitscherlich pulp, of the acetylated rag stock, and of the unacetylated rag stock were soaked for four hours in acetone. These samples were then treated in the British disintegrator according to standard procedure, with the exception that acetone was substituted for water. The disintegrated material was thickened to 600 cc. on a filter paper in a Büchner funnel and then beaten in the Lampén mill according to standard procedure.

The unacetylated rag stock was beaten for 45 minutes, the acetylated Mitscherlich pulp was beaten for 10 and 30 minutes, and the rag stock was beaten for 0, 15, 30, and 45 minute intervals. The beaten materials were then cleared in the British disintegrator for two and a half minutes and made into sheets in the usual manner, using acetone as the medium. The acetone was collected from the effluent of the sheet machine and reused for the subsequent preparation of sheets. The sheets were pressed, dried, conditioned, and tested according to standard procedures.

DISCUSSION OF RESULTS

The rag stock was apparently wet by the acetone, for it sank to the bottom of the container when the stock was soaked, whereas acetylated rag stock floated in water. However, when the unacetylated rag stock was processed in acetone in the British disintegrator, the fiber clumps were not defibered, and even after 45 minutes of beating

in the Lampén mill, many of these clumps still held together. The beaten material was cleared in the British disintegrator and an attempt made to form sheets with acetone as the medium; however, the resulting sheet was merely a bulky group of fiber clumps which would not hold together.

The acetylated Mitscherlich pulp and the acetylated rag stock both were wet readily by acetone, and both were completely defibered in the British disintegrator. Bletsinger noted that with his rag stock in acetone there was very little difference in the refractive index of the acetone and the fiber. In the present investigation, however, both the acetylated rag stock and the acetylated Mitscherlich pulp had refractive indices considerably different from that of the acetone.

The strength results of the acetylated rag stock beaten in water and in acetone and of the unacetylated rag stock beaten in water are given in Table XII and Figure 7. These results show that, when acetylated rag stock is beaten in acetone, it develops strength properties similar to those developed by beating rag stock in water. The sheets made from acetylated rag stock beaten in water had practically no strength—that is, by covering up about 37 per cent of the hydroxyl groups of the rag stock with acetyl groups, the bonding forces between the fibers were so reduced that all of the papermaking properties of the material were lost. When the acetylated rag stock was beaten in acetone, however, it developed strength properties considerably higher than those obtained by beating unacetylated rag stock in water. Although the strength values obtained in the present in-

vestigation were not nearly as high as those obtained by Bletzinger by processing fibrous cellulose acetate with 25 per cent acetyl content in acetone, they show that the acetylated material does bond together in acetone to produce a very good sheet.

The bursting strength of the acetylated rag stock beaten in acetone was about ten per cent higher than that of the rag stock beaten in water, and the tearing strength of the acetylated rag stock was about 20 per cent higher than that of the rag stock. The apparent density of the rag stock beaten in water was very much greater than that of the acetylated rag stock beaten in acetone. The sheets of acetylated material, therefore, are stronger than are the sheets of unacetylated material and at a much lower apparent density. That is, although it contained fewer fiber-to-fiber contacts, the acetylated material still had greater strength than the unacetylated material. Thus it appears that the bonding forces arising between acetyl groups at each fiber-to-fiber contact are stronger than those arising between hydroxyl groups.

The strength results obtained by beating Mitscherlich pulp in water and by beating acetylated Mitscherlich pulp in water and in acetone are also given in Table XII. The acetylated Mitscherlich pulp with 23.26 per cent acetyl content had very little strength when it was beaten in water, but the same material beaten in acetone gave sheets of very good strength. The bursting strength of the acetylated Mitscherlich pulp beaten in acetone was lower than that of the unacetylated Mitscherlich pulp beaten in water, but the tearing strength of the acetylated material was considerably higher than that of the unacetylated material.

TABLE XII

SUMMARY OF STRENGTH RESULTS OF MATERIALS BEATEN IN ACETONE

Observed Values

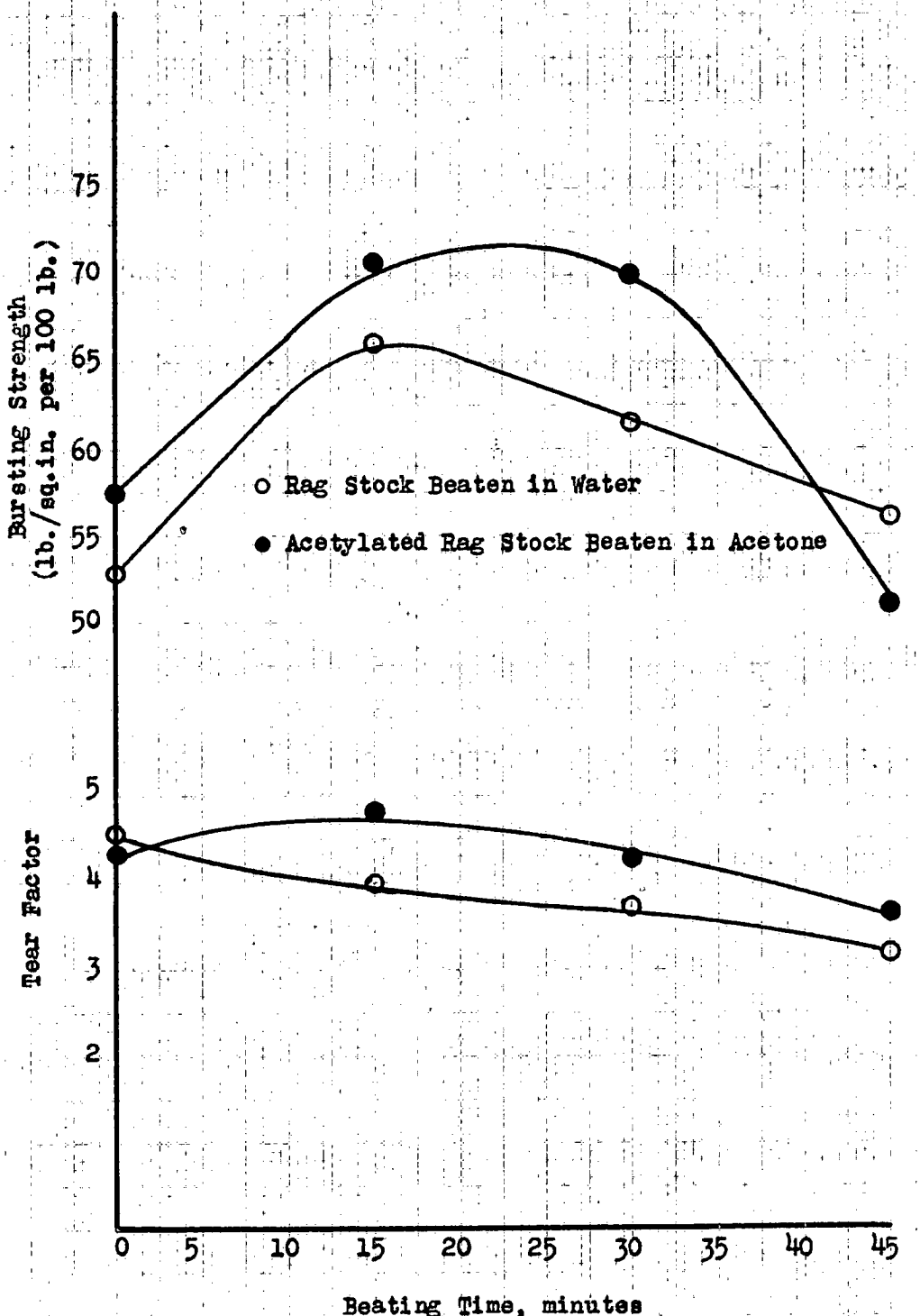
Material	Acetylated Mitscherlich pulp		Acetylated rag stock			
Beating time, min.	10	30	0	15	30	45
Basis weight	53.29	63.22	60.77	57.65	52.67	57.10
Caliper	4.60	5.45	8.24	7.27	6.50	6.10
Apparent density	11.80	11.60	7.37	7.93	8.10	9.51
Burst factor	64.17	89.69	44.60	54.64	54.11	39.58
Tear factor	1.285	1.075	3.317	3.717	3.301	2.995

Strength Values Calculated to Cellulose Basis

Beating Time	Basis Weight	Caliper	Apparent Density	Burst Factor	Tear Factor
		Mitscherlich Pulp Beaten in Water			
10	44.18	3.19	13.85	145.3	1.172
30	43.41	3.00	14.47	154.3	0.988
		Acetylated Mitscherlich Pulp Beaten in Water			
10	41.11	5.53	7.43	5.3	0.389
40	39.77	5.13	7.75	7.3	0.269
		Acetylated Mitscherlich Pulp Beaten in Acetone			
10	41.18	4.60	8.95	85.5	1.663
30	46.86	5.45	8.96	116.3	1.392
		Rag Stock Beaten in Water			
0	44.45	5.6	7.94	52.3	4.490
15	40.00	4.7	8.51	66.5	3.970
30	43.00	4.7	9.20	62.8	3.700
45	43.35	4.3	10.10	56.1	3.160
		Acetylated Rag Stock Beaten in Water			
45	41.56	6.48	6.41	2.41	0.212
		Acetylated Rag Stock Beaten in Acetone			
0	46.88	8.24	5.55	57.8	4.300
15	44.47	7.27	6.12	70.8	4.796
30	40.63	6.50	6.25	70.1	4.280
45	44.05	6.10	7.22	51.1	3.610

FIGURE 7

STRENGTH RESULTS OF ACETYLATED RAG STOCK BEATEN IN ACETONE COMPARED WITH THOSE OF RAG STOCK BEATEN IN WATER



At the ten-minute beating interval, the Mitscherlich pulp beaten in water had a bursting strength of 145.3 lb./sq.in. (per 100 pounds basis weight) and a tear factor of 1.172 as compared with a bursting strength of 55.5 lb./sq.in. and a tear factor of 1.663 for the acetylated material beaten in acetone. At the thirty-minute beating interval, the Mitscherlich pulp had a bursting strength of 154.3 lb./sq.in. and a tear factor of 0.955 as compared with a bursting strength of 116.3 lb./sq.in. for the acetylated material beaten in acetone. It will be noted that there is a greater increase in the bursting strength in the acetylated material from the ten- to thirty-minute beating intervals than for the Mitscherlich pulp for the same period. Also, it will be noted that, at both beating intervals, the tearing strength is higher in the case of the acetylated material. Both of these facts indicate that the acetylated Mitscherlich pulp beaten in acetone did not develop its strength upon beating as rapidly as did the unacetylated Mitscherlich pulp beaten in water; if the acetylated material had been beaten longer it might have developed strength values comparable with those developed by the unacetylated pulp beaten in water. The difference in rates of development and in the resulting strength values were probably due to the difference of pentosan content of the two materials. The unacetylated Mitscherlich pulp had a pentosan content of 5.7 per cent, whereas that of the acetylated pulp had been reduced to 3.9 per cent by the acetylation process.

Bletzinger's observations regarding water-repellent properties and fastness to ink were confirmed. The sheets prepared from acetylated rag stock (23.5 per cent acetyl content) in acetone floated on water and took ink like a well-sized sheet.

THEORETICAL DISCUSSION AND SUMMARY

The results of the present investigation may be utilized to substantiate and expand existing hypotheses on the actions that occur in the beating process and with regard to the bonding forces that hold a sheet of paper together.

The hypothesis that the bonding forces in a sheet of paper arise through the hydroxyl groups of the cellulose has been confirmed and expanded. Experiments with both rag stock and Mitscherlich pulp showed that, as the hydroxyl groups of the materials are covered with acetyl groups, there is an initial increase in the bonding forces and then a rapid decrease in the strength of the sheets made from the materials until, when about thirty-seven per cent of the hydroxyl groups have been covered by acetyl groups, the materials have practically no bonding strength. The hygroscopicity of a cellulosic material has been shown by other investigators to decrease with the decrease in number of available hydroxyl groups. In both the acetylated rag stock and the acetylated Mitscherlich pulp the hygroscopicity of the materials were found to have a direct relation to the strength properties.

These results indicate that the introduction of a small amount of acetyl content into the pulp apparently opens up the internal structure of the fiber to expose more hydroxyl groups for water binding. When this material with its increased number of available hydroxyl groups was beaten and made into a sheet, it had more water intimately held by the fibers than did the unacetylated pulp.

When the water was removed from the sheet by drying, the fibers of the slightly acetylated pulp, because they were more thoroughly wet by the water, were drawn into a more intimate contact, resulting in the production of a stronger sheet of paper. The introduction of a small amount of acetyl into Mitscherlich pulp also caused an increase in strength--however, it was not as great as that produced in the rag stock by the introduction of a corresponding amount of acetyl. This was probably due to the fact that some of the pentosan content in the Mitscherlich pulp was removed by the acetylation process.

After the initial increase in strength of the pulp upon the introduction of a small amount of acetyl, the introduction of more acetyl brought about a rapid decrease in the strength and water-binding properties of the pulp. In this case, the covering of the hydroxyl groups by acetyl groups was more important than the initial opening up of the fiber structure and, as more of the hydroxyl groups were covered, the material became more hydrophobic. When these more highly acetylated pulps were beaten and made into sheets, the fibers had less water intimately bound and, as the water was removed from the sheet (and the fibers were less wet by the water), the surface tension of the water did not draw the fibers into as intimate contact as it did with the unacetylated fibers, resulting in less bonding.

The results of the present investigation are in keeping with the theory of beating advanced by Campbell (8). According to Campbell, the purpose of beating is to increase the surface of the fiber by fibrillation and to reduce the mean fiber size, thereby reducing the rigidity of the fiber. When the sheet dries, the surface

tension of the water between the fibrous elements draws the flexible fibers into intimate contact and they are held together by the molecular attraction of cellulose for cellulose; this attraction has been shown by Bletzinger as well as by the present investigation to arise from the hydroxyl groups of cellulose.

Doughty (7) found that, after a small degree of beating had been accomplished, the effects of further beating could be brought about by pressing the wet sheet. Further beating or pressing caused an increase in apparent density, and the increase in tensile strength of the material was a straight line function of the apparent density. From Doughty's work one might draw the conclusion that the major factor in bonding is fiber-to-fiber contacts. Although this factor is important, a bonding force must be present also to render these contacts permanent. That this is true is shown by the results of the present investigation. The plot of tensile strength of the unacetylated Mitscherlich pulp against its apparent density gave a straight line relationship, as did the plot of the tensile strength of the acetylated Mitscherlich pulp (15.47 per cent acetyl) against its apparent density. In the latter case, however, the plot gave a much steeper curve than in the former case, indicating that, for a corresponding change in apparent density, the acetylated material gave a much lower increase in strength than did the unacetylated material. The unacetylated material, therefore, must have greater bonding forces per fiber-to-fiber contact than the acetylated pulp. These greater bonding forces arise from the greater number of hydroxyl groups in the unacetylated material.

That the beating medium must exert a swelling and wetting action upon the fibers so that, when the medium dries from the sheet, unsatisfied forces would be left to bond the fibers together into a sheet, was shown by Bletzinger's and the present study of processing acetylated rag stock in acetone. When acetylated rag stock (23.5 per cent acetyl) was beaten in water, the fibers were not wet by the water and no swelling of the fibers occurred. Thus, when the water dried from the sheet, no forces left by the removal of water from the hydroxyl groups of the cellulose were operative to bond the fibers together. The result was a sheet with practically no strength. However, when this same acetylated material was beaten in acetone, it gave strength development curves similar to those obtained when unacetylated rag stock was beaten in water. The acetone wetted and swelled the cellulose acetate and, when the acetone dried from the sheet, the attracting forces which were previously involved in the combination between the acetyl groups of the acetylated fibers and acetone became free for direct attraction and for the bonding of the fibers. The resulting sheets had strength properties even greater than those of the unacetylated rag stock beaten in water, although the apparent density of the sheets was little more than that of the acetylated material when it was beaten in water.

The acetylated materials with about 37 per cent of their hydroxyl groups covered by acetyl groups had practically no paper-making properties when beaten in water. It appears, then, that the bonding forces holding a sheet of paper together arise from about one-third of the hydroxyl groups of the cellulose.

It is interesting to speculate upon which of the hydroxyl groups are responsible for the strength development. In cellulose both types of hydroxyl groups may be free for bonding—i.e., the primary group in the 6-position of the anhydroglucose chain and the secondary groups in the 2- and 3-positions. Two possibilities must be considered. (1) The strength properties may arise from the hydroxyl groups in either the primary position alone, the secondary groups alone, or the secondary groups in either the 2- or 3-position alone. (2) The strength properties may arise equally from primary and secondary groups. There is some evidence in support of both possibilities.

Chippindale (34), by the use of dyestuffs which dye cellulose acetate but do not dye cellulose, has shown that the course of the acetylation of cellulose with retention of the original fiber structure is different from that in the preparation of cellulose acetate by the methods usually applied in industry. Commercial acetylation may be regarded as proceeding in a topochemical manner. When fibers are partially acetylated by this method and are dyed with cellulose acetate dyes, only the outer part of the fiber cross section is colored. It appears that upon immersing the cellulose in the acetylation bath the outer layer of the fiber is attacked first and is acetylated possibly as far as the triacetate stage with the interior part remaining unaltered. After swelling and solution of this layer, the next layer of unacetylated cellulose is available for acetylation. This process continues until the fiber is completely acetylated to the triacetate stage.

If mild conditions of acetylation are used, however, the reaction is shown to be permutiedal, for cellulose acetate dyes show that the fibers acetylated in this manner are colored throughout. Chippindale states that, by a mild method of acetylation, mono- and dicellulose acetates can be prepared, but he does not express an opinion as to whether the cellulose mono-acetate has covered up only primary hydroxyl groups, only secondary acetates, or a mixture of the two.

The cellulose acetates in the present study were prepared by a very mild method of acetylation. Indeed dyeing of the material of 10.36 per cent acetyl content with cellulose acetate dyes showed the material to be colored uniformly throughout the cross section of the fibers.

In an attempt to explain why cellulose acetate containing 2.1 to 2.6 acetyl groups per anhydroglucose residue is soluble in acetone if prepared by partial hydrolysis of triacetate, but is insoluble in acetone if the acetate is acetylated directly to this acetyl content, Cramer and Purves (35) concluded that the solubility depends not only upon the hydroxyl to acetyl ratio but also upon the relative distribution of the hydroxyl groups. Treatment of commercial secondary (acetone-soluble) cellulose acetates with tosyl chloride and sodium iodide showed such acetates to have from 35 to 50 per cent primary hydroxyl groups. Tosylation proceeded rapidly at first and then decreased; the plot of the degree of tosylation against time gave rate curves very similar to those obtained by plotting the degree of acetylation of fibrous cellulose acetate against time. Samples

of the tosylated materials, taken at various intervals and treated with sodium iodide, showed that the rate of tosylation of the primary groups was eleven to twelve times as great as that of the secondary groups. Thus, the initial rapid rate probably occurred while the primary groups were being tosylated, and then slowed down while the secondary groups were tosylated.

In a like manner, the acetylation of fibrous cellulose may be fast at first due to the acetylation of primary groups and, after these groups are acetylated, the rate may slow down. In the present study only about 37 per cent of the hydroxyl groups of the cellulose were covered by acetyl groups in 42 days. If this 37 per cent included all of the primary hydroxyl groups, it would be logical to assume that bonding forces between (unacetylated) fibers arise through their primary hydroxyl groups. A study of the distribution of the primary and secondary hydroxyl groups in the acetylated cellulose acetates prepared in the present study was considered, but the method used by Cramer and Purves required ten days for a 75 per cent tosylation of about one-sixth of the hydroxyl groups originally present in the cellulose. Moreover, the material with which they worked was of short chain length, as shown by its solubility in pyridine, in which the tosylation was carried out, and it is probable that the long chain material used in the present investigation would take a much longer time. Some modification of this method which could be used with long-chained fibrous cellulose acetate might give results that would be of significance in this problem.

That the bonding strength of cellulose might be due to both primary and secondary hydroxyl groups is indicated by the work of Mark and Meyer (33). These investigators have calculated that 30 to 50 per cent of the hydroxyl groups of cellulose are present on the micelle surfaces. Hess (36) has found that, upon acetylation of cellulose, no change in the x-ray diagram occurred until 47.7 per cent of the hydroxyl groups were covered by acetyl groups. It is probable, therefore, that the forces which bond the cellulose fibers together arise from hydroxyl groups on the micelle surfaces. The mild method of acetylation used in the present investigation probably acetylates chiefly the surface hydroxyl groups, thus destroying the papermaking properties of the cellulose.

Several investigators have reported that pentosans either originally present in the pulp, or added to the pulp in the beater, improved the strength of the sheets made from the beaten pulp. The results of the present investigation show that the beneficial effect of the presence of pentosans materializes only if the attractive forces exerted by the surface hydroxyl groups of the cellulose and by those of the pentosan can operate to produce combination with water and thus bring about the conditions which are requisite for subsequent direct bonding between the respective hydroxyl groups. If, however, these hydroxyl groups--that is, either those in the cellulose or those in the pentosan which are involved in the reaction with water--are covered by acetyl radicals, the reaction with water and the possibility of subsequent direct bonding are prohibited. On the other hand, the attractive forces between the acetyl groups of cellulose and the

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the acetyl groups of the acetylated fiber (witho[illegible]rted by
addition of pentosan) in the acetone medium. [illegible]nce or

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