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Doctor's Dissertation

The Investigation of the Physical Properties and the Reactivity and the Hygroscopicity of Acetylcellulose Preparations from Neutralized Toluene

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THE INVESTIGATION OF THE PHYSICAL STRENGTH PROPERTIES,
THE HYDROSCOPICITY AND THE HYDROEXPANSIVITY
OF HANDBRACKS PREPARED FROM
ESTERIFIED PULP FIBERS

A thesis submitted by

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INTRODUCTION

The work of Bletzinger (1) and Aiken (2) (which, together with other publications, is reviewed in the next section of this thesis) has demonstrated the role which is played by the hydroxyl groups of cellulose in the beating and sheet-forming processes of papermaking. The relation between the physical strength properties of sheets prepared from partially acetylated cellulose fibers and their acetyl content, established by Bletzinger, was extended by Aiken to include the hygroscopic properties of acetylated fibers.

It could be expected that the relation which was thus established between the physical strength properties and the hygroscopicity for partially acetylated fibers would also hold for sheets prepared from partially acetylated fibers which had been merely disintegrated without actually beating in water. In the present investigation, in which bleached Mitscherlich pulp was used exclusively as the raw material, this was found to be true. In this part of the present investigation, there has been included a study of the influence of the temperature upon the rate of acetylation, using acetic anhydride and pyridine. The object was to increase this rate, and thus to shorten the extremely long time required by this method to reach even a medium degree of substitution. With the same object in mind, a comparison was made between this method and that using acetyl chloride and pyridine.

The reduction of the hygroscopic properties of cellulose fibers, by partial acetylation, indicates that the hygroexpansivity of sheets prepared from acetylated fibers would also be reduced, because
both properties depend upon the ability of the fibers to absorb water. In the present investigation, such a study was undertaken with sheets prepared from bleached *Miscellanea* pulp of increasing esteryl content, and the results were compared with the hygroscopic and the physical strength properties of these sheets. If the water-binding properties of cellulose, the bonding strength developed in paper, and the hydroexpansivity are all dependent essentially upon the hydroxyl groups of cellulose, this study could be expected to show a direct correlation between these three characteristics. In this connection, attention was also paid to the possibility of a commercial utilization of paper of a reduced hydroexpansivity prepared from partially esterified fibers.

In view of the fact that the hygroscopicity of cellulose esters decreases with the chain length of the acyl radical introduced, it seems logical to expect that the other sheet characteristics, mentioned previously, would also be influenced by the chain length of the acyl radical. Thus, with the introduction of longer chain acyl radicals, rather than the acetyl radical, lower degrees of substitution could be expected to produce similar effects on the cellulose fibers. Such studies were accordingly undertaken with partially butyrylated and partially stearoylated *Miscellanea* pulp fibers and the relation of the three sheet characteristics established.

In addition, attempts were made to utilize acetone and other organic liquids as processing mediums for the acetylated, butyrylated, and stearoylated pulps.
The effect of esterification upon the water-binding capacity of cellulosic materials has long been a subject of investigation. Sheppard and Newsome (1, 4), in particular, made extensive studies of absorption of water by cellulosic materials and cellulose acetates at various vapor pressures and found that the hygroscopicity of cellulose fibers decreased in an almost linear manner with the acetyl content. More recently, these investigations of Sheppard and Newsome were extended by Bleizinger (1), by Brown and Harrison (5, 6), and by Aiken (2), and the effect of the hydroxyl groups of cellulose upon its paper-making properties was ascertained. Summaries of the literature, as it pertains to the role of the hydroxyl groups of cellulose in the sorption and desorption of water as well as in the beating process, were presented by Bleizinger (1) and by Aiken (2), so that a discussion of the more general aspects will not be included here.

Bleizinger (1) studied the effect of hydroxyl groups on the bonding strength of paper by covering part of the hydroxyl groups with acetyl groups, using an esterification method which left the cellulose fibers practically undegraded. In the course of this investigation, he discovered that, during the initial stages of substitution, the physical strength properties of beaten rag stock increased and reached a maximum at an acetyl content of about 5 per cent. With further increasing acetyl content, however, the physical strength properties decreased rather rapidly and reached almost zero values with an acetyl content of about 25 per cent. The initial increase and subsequent decrease in physical strength properties were explained as follows.
The introduction of acetyl groups increased the distances between adjacent cellulose chains in the micellar system so that, on beating, a greater number of available hydroxyl groups were exposed to water than would have been in the case of the unacetylated cellulose fibers. Thus, the extent to which the acetylated fibers underwent hydration increased with increasing acetyl content up to a certain point. As a result, the bonding between adjacent fibers increased as the water was removed, and the physical strength properties of the sheets thus formed were improved. However, this effect becomes noticeable only up to a certain acetyl content; beyond this point, the influence of the hydrophobic character of the acetyl groups becomes more and more predominant and thus subordinates the increased hydration effect and subsequent improved bonding. Consequently, the physical strength properties decrease and become almost zero when a certain acetyl content has been reached.

The incompatibility of the partially acetylated fibers with water suggested that, by the use of an organic liquid as a beating medium, which would swell the acetylated fibers (without dissolving them), a coherent and strong sheet of paper may be obtained. Acetone proved to be a suitable beating medium, and its use resulted in the preparation of sheets of excellent physical strength properties. These properties were even superior to those which were produced by beating unacetylated rag stock in water. In addition, the sheets thus prepared were resilient to water and to ink to a remarkable extent.

Aiken (2) working with both acetylated rag stock and wood
pulp, confirmed and extended the hypothesis presented by Blotsinger
and also demonstrated that the direct relationship which could be ex-
pected to exist between the physical strength properties and the
hygroscopicity of partially acetylated pulps actually existed. In
addition, it was found that the characteristic curve in physical
strength properties with increasing acetyl content was obtained merely
by subjecting the cellulosic material to a certain measure of disin-
tegradation (i.e., without actual beating) and that the hygroscopicity
maximum occurred with the acetylated fibers which had not even undergone
a process of disintegration. Thus, it would appear that the mere
opening of the micellar structure of the fibers which results from
acetylation (i.e., without beating) suffices to increase the number of
accessible hydroxyl groups, which permits the fibers to absorb more
moisture from the surrounding atmosphere. Again, with further increasing
acetyl content, the fibers become more and more hydrophobic and, as a
result, the hygroscopicity and physical strength properties drop. Aiken
also confirmed the development of strength properties by beating the
acetylated materials in acetone, although he did not obtain as high
strength values as were shown by the unacetylated material when beaten
in water.

Brown and Harrison (5, 6), hoping to produce a paper of high
insulating properties by covering the hydroxyl groups with acetyl
groups, found that the physical strength properties and the moisture
content of acetylated kraft pulp decrease rapidly with increasing acetyl
content. However, it may be mentioned here that they did not observe
the phenomenon of an increase in the physical strength and hygroscopic
properties within the range of very low acetyl contents.

The results of the studies by Bletzinger and by Aiken appear to be in good agreement with the ideas which Campbell (1, 3) has advanced on the mechanism of beating and sheet formation. According to Campbell, the "physical" 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. Thus, conditions are produced which are favorable to the formation of a sheet when the water is removed. When the sheet is dried, the surface tension of the water between the fibrous elements draws the flexible fibers into intimate contact so that the molecular attraction of cellulose for cellulose comes into play, this attraction being attributed to the hydroxyl groups of the cellulose. If a number of the hydroxyl groups are replaced by acetyl groups, the acetylated fibers become incompatible with water and thereby impede hydration and subsequent bonding between adjacent fibers. If, however, the water is replaced by acetone, the acetyl groups become solvated. When the acetone is removed, the acetyl groups are drawn closely together so that the forces of mutual attraction become operative and bonding can occur.

Sheppard and Newsome (4) and Hagedorn and Föller (2) have shown that the chain length of the fatty acid radical which is introduced into cellulose has a considerable effect upon the hygroscopic as well as the physical strength properties of the fibers so modified. Sheppard and Newsome (4), investigating the percentage of moisture regain (at 100 per cent relative humidity) of various triesters, found these values to
decrease with the length of the acid chain radical. The moisture regains were as follows: For the triacetate—10 per cent, the trimethylacetate—4.14 per cent, the tributyrate—3.5 per cent, the trivalentate—1.7 per cent, and for the tributoxycetate—0.3 per cent. Previously, Hagedorn and Müller (2) had shown that, as the carbon chain of the acyl group became longer, the tensile strength of films prepared from the various cellulose esters decreased rather rapidly to a minimum value with the tristearate, which gave a tensile strength of only 0.5 kg./sq. mm. compared with 10 kg./sq. mm. for films prepared from the triacetate.

Mention must also be made of the work of Weidner (10), who studied the influence of humidity changes of the surrounding atmosphere upon the diameter and the length of sulfite pulp fibers. He found a fundamental correlation between the moisture content and the dimensions of individual fibers. In addition, it was shown that bleaching, beating, and oven drying decreased the swelling of the fiber markedly, with only a very slight decrease in moisture sorption. The shape of the curves expressing fiber diameter as a function of relative humidity was similar in all cases. However, when hygroexpansivity measurements on sheets from unbeaten and beaten pulp were compared, it was found that the change for a given humidity change was greater for the beaten than for the unbeaten sheets, in spite of the fact that the individual beaten fibers were previously found to swell less. The explanation for this result was based upon the assumption that in the beaten sheet there is more fiber-to-fiber bonding, thus giving rise to a denser sheet. The denser sheet would cause the expansions and contractions of the
individual fibers to be transmitted more positively to the sheet and thus cause a greater over-all change in sheet dimensions.

In addition, attention may be directed to the work of Velkov and Cobb (11), who found that the dimensional changes which paper undergoes with a change in moisture content show the hysteresis effect.

Finally, various TAPPI reports (12), in which the changes occurring in a sheet of paper with humidity changes are discussed more generally, may be mentioned.

EXPERIMENTAL PROCEDURES AND METHODS

RAW MATERIAL

Fifty pounds of bleached kraft sulfite pulp, which had been obtained from a local pulp mill in wet lay form, were placed in one of the experimental blowpipes with water and mixed thoroughly for 1 hour. The excess water was drained off, the pulp was pressed in a wine press, torn into small pieces, and spread out to air dry. The dried material was sampled for moisture tests and stored in sealed glass jars.

The average degree of polymerization of the pulp, determined by StAUDINGER's method, was found to be 1653.

METHOD OF ACETYLATION

The acetylations of the pulp were carried out by the method of Hess and Ljudite (13); this procedure had previously been shown by HECSTRINGER (1) to cause little or no degradation. To eliminate the
effect of mercerization and possible oxidation, Bletzinger omitted
the steeping of the cellulose (and removal of the alkali) before
placing the pulp in the acetylation mixture of pyridine and acetic an-
hydride. Bletzinger's results showed that this modified method of
acetylation did not reduce the tensile strength of the individual
fibers and did not change the degrees of polymerization appreciably.
Moreover, pulp regenerated from the acetylated fibers prepared by this
method had practically the same characteristics as the original cellulose.
Aiken (2) used this procedure for preparing acetylated rag and wood
pulp samples, and the same method was also employed in the present in-
vestigation.

The details of the method are as follows: Witscherlich pulp
(equivalent to 150 grams of oven-dry material) was placed in a 1-gallon
glass-stoppered jar, covered with pyridine, and allowed to soak over-
night to remove moisture from the pulp and to swell the fibers. The
pulp was defibered for 5 minutes by means of a Lightnin' mixer, and
feed of
the pyridine was removed on a Buchner funnel. Between 250 and 400 ml.
of pyridine remained in the pads. The pulp was weighed and returned
to the jar, the calculated amount of pyridine-acetic anhydride mixture
was added, and the mixture was stirred for 10 minutes before setting
aside.

The acetylation mixtures were prepared either by the addition
of fresh acetic anhydride to the acetylation mixtures recovered from
previous acetylations or by the use of a fresh mixture of acetic an-
hydride and pyridine. The total acetylation mixture, including
pyridine remaining in the pulp pad, amounted to 10 ml. of acetic anhydride and 15 ml. of pyridine per gram of oven-dry pulp or a 33.4 per cent acetic anhydride mixture by volume. Acetylation mixtures were never used for more than two acetylations in this investigation.


The acetyl content of the product was controlled by the time of exposure, the temperature, and the concentration of the acetic anhydride in the materials, left in contact and by the temperature. The temperature was 240° C. up to an acetyl content of about 15 per cent. In spite of the relatively low temperature, the rate of acetylation with this method is rather rapid for the first few minutes, after which it decreases considerably. The acetylates with acetyl contents above 15 per cent were removed by placing the suspension of the pulp and the acetylation mixture in a water bath at 140° C. The time the pulp were in contact with the acetylation bath varied from a few minutes to many days.

At the end of the esterification period, the acetylation mixture was removed from the product by filtering the suspension through a Büchner funnel; the filtrate was saved for future acetylations. The acetylated pulp pad was transferred to a 4-liter beaker and was washed three times with pyridine to remove the red color formed during the acetylation. The pyridine was removed by three washings with ethanol, and the alcohol was removed by three washings with ether. Air was sucked through the pad for several minutes to remove the ether, and the materials were finally torn into shreds and allowed to dry in the air for several hours before they were stored in sealed jars.

In the shorter acetylation periods, no red color was formed.
in-the-esterification-mixture; therefore, the washing with pyridine was omitted, the material being washed immediately with alcohol and ether and then dried in the usual manner.

For the preparation of the products of low acetyl content, the procedure was modified by decreasing the concentration of the acetic anhydride in the acetylation mixture, the temperature being maintained at 210°C. In this way, the initial rate of reaction was reduced. The volume of the acetylation mixture was kept constant. The methods of stirring and washing were the same as in the regular procedure. Ten minutes were allowed for the removal of the acetylation mixture on the Büchner funnel, and the time of acetylation was measured from the addition of the acetylation mixture to the jar until the end of the suction time on the Büchner funnel.

Table I presents a summary of the acetylation conditions, the acetyl contents of the acetylated fibers, and the percentage of free hydroxyl groups of cellulose covered by acetyl groups.

In addition, the table contains data for a sample which had been in contact with the acetylation mixture for 239 days (Aiken, 2). In spite of this long period of time, its acetyl content was only 33.1 per cent—i.e., not very much higher than that of a sample (Table I) which had been in contact with the acetylation agents for only 42 days. It thus appears that it is not possible to reach the triacetate stage within any reasonable time; the reason that the product of Hess and Ljubitsch approached the triacetate stage after 14 weeks was because of the swelling effect resulting from the pretreatment of
### TABLE I

Acetic Anhydride, % by Volume | Time | Temperature, °C | Apparent Acetyl, % | Hydroxyl Groups Covered, %
--- | --- | --- | --- | ---
2.5 | 70 min. | 24 | 2.52 | 3.2
5.0 | 65 min. | 24 | 2.64 | 3.4
7.5 | 70 min. | 24 | 4.65 | 6.12
20 | 55 min. | 24 | 4.7 | 6.19
5 | 6 hr. | 24 | 5.37 | 7.32
38.4 | 45 min. | 24 | 8.9 | 12.24
38.4 | 70 min. | 24 | 10.05 | 13.99
20 | 70 min. | 24 | 10.66 | 14.85
38.4 | 6 hr. | 24 | 13.57 | 17.99
38.4 | 10.25 hr. | 24 | 14.5 | 21.21
38.4 | 63 hr. | 24 | 15.87 | 23.59
38.4 | 13 days | 40 | 13.1 | 27.6
38.4 | 43 days | 40 | 20.1 | 31.4
(‘water leaked in during last 3 or 4 days’)
38.4 | 42 days | 40 | 25.65 | 43.0
--- | --- | --- | --- | ---
38.4 | 239 days | 40 | 33.1 | 61.5

*Experiment by Alken (2)*
the cellulosic material with strong alkali. It is also possible that the cellulose had been degraded during this pretreatment.

ACETYL AND BUTYRYL DETERMINATIONS.

After a thorough investigation of the methods for determining the acyl content of cellulose esters, Gemung and Hallatt (14) found a modification of the Eberstadt method to be the most accurate for acyl groups up to and including the butyrate. In this method, the cellulose ester is saponified with alcoholic sodium hydroxide after swelling in 75 per cent ethanol; however, swelling in alcohol is not always necessary. The time necessary for complete saponification is 16 to 24 hours with 0.25 N sodium hydroxide and a temperature not exceeding 35° C. The method has a precision of ±0.25 per cent of the numerical value and an accuracy of ±0.5 per cent of the numerical value obtained.

The procedure used in this investigation was that of Gemung and Hallatt (14) with minor modifications in sample size and amounts of solution. One-half gram of oven-dry material was placed in a 250-ml. Erlenmeyer flask, 25 ml. of 75 per cent ethanol were added, and the sample was digested for 30 minutes in a water bath at 50° to 60° C. Twenty-five ml. of 0.5 N sodium hydroxide were then added from a pipet, the flask loosely stoppered, and the contents digested in a water bath at 50° to 60° C. for 15 minutes. The flask was then tightly stoppered and was allowed to stand for 36 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 1 per cent phenol-sulfalein solution were added, and the excess
alkali was titrated with standard 0.1 N hydrochloric acid, adding a slight excess. After allowing 2 to 4 hours for the alkali to soak out of the fiber, the excess acid was back-titrated with 0.1 N sodium hydroxide to a phenolphthalein end point. The amount of acid was corrected for the alkali required to establish the end point, and the percentage of acyl was calculated. All the determinations were run in triplicate. The percentage of acyl was calculated according to the following equation:

\[ \% \text{ acyl} = \left(\frac{(\text{ml. alkali consumed}) (N) - (\text{ml. acid}) (N) \text{ equivalent weight}}{\text{sample weight} \times 10} \right) \times 100 \]

The equivalent weights used were: acetyl 1.3, butyryl 71.1.

STEARYL DETERMINATION

The method of Gemung and Wallatt (14), developed for the determination of the acyl content of higher fatty acid esters of cellulose up to and including the stearates, consists of subjecting the esters to a saponification procedure with an excess of 0.25 N alcoholic sodium hydroxide solution followed by titration of the unused alkali with 0.25 N hydrochloric acid, using phenolphthalein as an indicator. When this method was applied to the cellulose stearates investigated in the present study, it soon became apparent that the values obtained were too high. The results seemed to indicate that some free acid (stearic or hydrochloric or both) had been retained by the esters. This situation did not change when, prior to the analysis, the stearates were subjected to a thorough extraction in a Soxhlet apparatus with alcohol, followed by an equally thorough extraction with ether, nor did various modifications of the method of saponification (using higher
alkali concentrations, higher temperatures, and longer times) improve the results. As an example, a stearate analyzed for its stearoyl content by the method of Gamung and Ballow yielded 68.2 per cent, whereas the value derived from an elementary analysis of the carbon and hydrogen content was only 40.3 per cent.

Other investigators, who apparently had experienced similar difficulties with the accurate estimation of the acyl content of higher fatty acid esters of cellulose, resorted to the direct isolation of the combined fatty acid. Therefore, it was decided to use this method in the present investigation. Although the values thus obtained were still somewhat higher than those derived from the elementary analysis, they were considerably lower than those found by the saponification method. The sample mentioned above yielded 57 per cent by the isolation method. It is also possible that the values derived from the elementary analysis are not very reliable. This is borne out by a communication from C. H. Fordyce of the Eastman Kodak Co. Fordyce also confirmed the difficulties encountered with the saponification method and favors the isolation method as the more reliable procedure. The values obtained by the isolation method checked within 1 per cent.

It must be kept in mind that a commercial stearoyl chloride was used in this investigation. According to verbal information received from the manufacturers, it is only 95 per cent pure, the rest being palmitoyl chloride (about 5 per cent) and oleic and other acid chlorides (about 1 per cent). The results of the stearoyl determinations are calculated upon the equivalent weight of pure stearic acid, and the values obtained thus represent "apparent" stearoyl contents.
In addition to the regular washing and extraction of the
steaerylated pulp, a sample of the air-dry steaerylated pulp, which
was to be analyzed, was extracted for 8 to 12 hours in a Soxhlet ex-
ntractor with ethanol. The ethanol extraction was followed by an
8- to 12-hour extraction with ether. These operations should remove
any free stearic acid from the sample. The pulp samples were then
dried in the air.

The procedure for isolating the combined stearic acid was
as follows: Approximately 15 grams of pulp were dried to constant weight
in a vacuum oven at 60°C. Fifty ml. of approximately 0.5 N alcoholic
cuporine hydroxide (per gram of oven-dry pulp) were added, and the
samples were allowed to stand at 50°C. for 24 hours. After this time,
the excess of alcoholic alkali was removed on a Buchner funnel, and
the sample was washed thoroughly with boiling alcohol. The sample was
then placed in a Soxhlet thimble and extracted for 16 hours with
acidulated alcohol. The regenerated cellulose was washed with water
until it gave no reaction with phenolphthalein. The water retained
in the pulp was displaced by washing with alcohol. Finally, the pulp
was extracted for 8 hours with ether. The alcoholic alkali and all
the extracts from the alcohol and water washes were then united and
evaporated just to dryness. The residue (the potassium salt of the
fatty acid) was dissolved in warm water and the solution acidified
with dilute hydrochloric acid. The free stearic acid which pre-
cipitated on acidification was extracted with ether. The ether layer
was then separated in a separatory funnel and the water layer extracted
twice more with ether. The ether solutions were combined and washed
three times with distilled water to remove any water-soluble free acid, such as hydrochloric acid. After the last wash, the ether extract was evaporated to dryness and dried to constant weight in a vacuum oven at 65°C. The weight of the residue was taken as the amount of alcohol-insoluble material. The combined acid-insoluble matter and the percentage of stearoyl content were calculated.

In order to determine whether the stearate was completely saponified by the treatment with alcoholic alkali, a sample of the regenerated pulp was subjected to the same treatment, using the isolation procedure. The stearic acid content of the regenerated pulp was found to be negligible. Elementary analysis of a pulp regenerated with 0.25 M alcoholic sodium hydroxide at 70°C confirmed this result, for it showed approximately the same carbon-hydrogen values as the original pulp. The carbon and hydrogen values for the regenerated cellulose were 43.24 and 6.95 per cent, respectively, whereas those for the original cellulose were 44.52 and 6.18 per cent. It was apparent from the ash determination (5.17 per cent) on the regenerated cellulose that some alkali had been retained from the saponification, even after the washing to which it had been subjected. The presence of the alkali partially explains the low carbon and hydrogen values for the regenerated cellulose. The carbon and hydrogen values of the regenerated cellulose, after correcting for the ash content, were found to be 45.55 and 6.77, respectively. These figures, compared with 44.52 and 6.18 for the raw material, indicate that about 0.34 per cent of the hydroxyl groups are covered by stearoyl groups or that about 2 per cent stearoyl radical is present in some other form. By the use of 0.5
A alcoholic potassium hydroxide at 50° C., which was specified for the standard procedure, it might be possible to obtain an even more complete removal of the stearoyl groups. However, it may be concluded from the above experiments that only a negligible amount of stearoyl radical remains after the standard saponification procedure with alcoholic potassium hydroxide.

DETERMINATION OF THE DEGREE OF POLYMERIZATION

The average degree of polymerization of the starting material, the acetates, and the butyrates were determined by measuring the specific viscosities in cuprammonium hydroxide solution, according to the method of Staudinger (15). The apparatus used and the procedure followed have been described by Heuser and Green (16). Air-dry acetylated and butyrylated pulp samples were employed. The data obtained were calculated on the oven-dry cellulose content of the esterified products. This was possible because both the acetates and the butyrates undergo saponification when they are dissolved in cuprammonium hydroxide. Thus, the viscosity is determined for the regenerated cellulose. This was found by Staudinger and Baumiller (17) to be true for cellulose acetates, and use was made of it by Bletsinger (1). In the present investigation, this behavior was established for the butyrates.

The cuprammonium solution was prepared according to the method of Lottermoser and Wultsch (13).

Heuser and Green have pointed out that, in the determination of the degree of polymerization of cellulosic materials in cuprammonium hydroxide solutions, a complete dispersion must be obtained. At this
point, the viscosity of the solution will be the highest. A subsequent drop in viscosity indicates a degradation of the cellulose. Hence, the change in viscosity with time must be observed in order to ascertain the maximum value. Once the approximate period for complete dispersion has been found, the viscosity is taken at that time; however, it must be checked 10 to 20 hours later.

Staudinger's equation has a constant ($K_s$) for calculating the molecular weight, the value of which is $5 \times 10^{-4}$. The degree of polymerization, as expressed in this dissertation, is equal to the molecular weight by Staudinger's equation divided by 162, and refers to the average degree of polymerization of the material.

Degree of Polymerization of the Stearates

The degree of polymerization of the stearates could not be determined by the Staudinger method, because neither the stearates nor the cellulose regenerated from them dissolved in cuprammonium hydroxide solution or the other solvents tried.

Several samples of the stearates were placed in cuprammonium solution and allowed to remain for several days. The samples did not dissolve nor did they appear to be even wetted during this time. An attempt to dissolve the stearates by wetting the fibers with a small amount of alcohol prior to the addition of the cuprammonium hydroxide solution was also unsuccessful. Fibers could still be observed after several days.

The cellulose was regenerated from the stearates by a saponi-
fication procedure with alcoholic alkali and subsequent washing, similar to that employed for the analytical determination of the stearoyl content. The regenerated fibers appeared to be wet readily by water. However, the regenerated cellulose did not dissolve in cuprammonium hydroxide solution even after several days at room temperature. It was thought that this might have resulted from the presence of a residue of combined stearic acid which had not been removed by saponification. However, it will be recalled that, according to the elementary analysis of the once saponified cellulose, practically all the stearic acid had been removed by this saponification.

The surprising behavior of the regenerated cellulose with cuprammonium hydroxide solution seemed to indicate that the cellulose had lost its reactivity; it was thought that the original reactivity could possibly be restored by a pretreatment. Various pretreatments were tried on the doubly saponified regenerated cellulose sample. First, a portion was soaked in concentrated ammonium hydroxide for 16 hours prior to the addition of the cuprammonium hydroxide solution. The sample showed no signs of dissolving, even after 5 days. Second, a sample of the regenerated pulp was placed in cuprammonium hydroxide and allowed to stand at -20°C for 16 hours before allowing the solution to rise to the normal dissolving temperature. The sample showed no signs of dissolving after 5 days at 25°C. Finally, a sample of the regenerated pulp was subjected to the vapors of acetic acid for 5 minutes. This treatment is said to restore the reactivity of mercerized cellulose and of alpha pulp used for acetylation. Cuprammonium hydroxide solution was then added to the acid-treated fibers, but the
fibers did not dissolve even on long standing.

Several attempts were made to dissolve the stearates in solvents other than cuprammonium hydroxide solution. Samples of a stearate with a stearoyl content of 55.4 per cent were placed in the following organic liquids: xylene, chloroform, carbon tetrachloride, benzene, monochlorobenzene, and m-cresol. The esters swelled in all these solvents but did not go into solution, even on long standing at room temperature. A sample of the stearate was placed in 85 per cent phosphoric acid, which has been used as a swelling agent in pretreatments of cellulose preparations by Staudinger and Kohl (19). However, the fibers were not even wetted by the acid but floated on the surface, even after standing for several weeks.

It would appear, therefore, that the insolubility of the stearic acid esters in cuprammonium hydroxide solution is a result, at least in part, of the presence of the long chain acid groups which prevent the fibers from being completely wetted and becoming accessible to the agents used for saponification and solution. However, the peculiar behavior of the cellulose regenerated from the stearates seems to indicate that the physical structure of the fiber has suffered an essential change during esterification. Without further experimental studies, it is difficult to discuss the nature of this change. Perhaps the introduction of the long acid chains has caused a change in the crystalline structure of the fiber, possibly in the degree of orientation of the micelles.
Of the various laboratory devices available for strength evaluation of pulp, the Hempel mill was chosen as the most desirable for the following reasons: It has been thoroughly tested, and the results have been found to be reproducible and to correlate well with results obtained by large-scale beating experiments. The procedure is fairly rapid, and only a small charge is required. Also, according to H. A. Harrison (20), reproducible results may be obtained in beating with a variation in charges between 18 and 24 grams, provided the consistency remains the same during beating.

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 (21) was followed, with the exception that, after disintegration, the pulp was concentrated by filtering on a Büchner funnel instead of using a screen thicker. A charge of 18 grams (oven-dry pulp basis) was used, and the consistency was maintained at 3 per cent. All the materials were soaked in the processing medium for at least 12 hours prior to beating.

A strength development curve was obtained for the original pulp by subjecting it to various degrees of beating. The intervals chosen were 0, 10, 20, 40, and 60 minutes. From this curve, it appeared that the maximum strength for the pulp in question was reached between 20 and 40 minutes. The postylated pulps were beaten for 0, 20, 40, and 60 minutes. In all cases, the maximum strength was found to be very close to the 40-minute beating interval.
Physical tests on the butyrated and acrylated pulps were made on handsheets prepared at the zero- and 10-minute beating intervals. Thus, all the materials could be compared under standard conditions.

The sheets prepared from the esterified pulps were formed, pressed, dried, and conditioned according to TAPPI Standards T 205 m-40. Likewise, the sheets were tested according to TAPPI Standard Methods for basis weight (T 410 m-41), caliper (T 411 m-36), and for tearing (T 414 m-40), bursting (T 403 m-36), and tensile strengths (T 404 m-41).

Trimmings from the tested sheets were used for the determination of the moisture content, and the basis weight was calculated to a 25 x 40 - 500 oven-dry basis. The basis weight of the esterified material was calculated on a ash-free basis to give a comparison of equal weights of fibers. The strength values were divided by the basis weight to reduce them to a common basis for comparison.

HYDROSCOPICITY MEASUREMENTS

The amount of water absorbed by the esterified and unesterified materials from the air at various relative humidities was determined by ascertaining directly the increase in weight of the cellulosic materials.

The method used for determining the changes in weight of the samples at the different humidities was one commonly employed and was essentially the same as that followed by Aiken (2).
The temperature of which was maintained at 73° ± 1° F. instead of at 86° F. A heating unit, controlled by a thermoregulator set at 72° F., was attached to the inside of the box to control the temperature in case the room temperature fell too low. The relative humidities were determined by the difference in temperature of a wet and dry bulb thermometer.

The samples for the hygroscopicity measurements were taken from handsheets which had been thoroughly conditioned. The wet handsheets were placed in the humidity room (maintained at 50 per cent relative humidity and a temperature of 73° C.) immediately after the last pressing and were allowed to come to equilibrium under these conditions. (The handsheets used for the hygroscopicity measurements were a portion of those which had been prepared for the physical tests.)

Because of the hysteresis phenomena observed with cellulose, the manner of approaching a given humidity may affect the moisture content of the sample. Therefore, the unacetylated and the acetylated pulps were subjected to absorption and desorption cycles. The samples were first conditioned at the lowest humidity and weighed, whereupon the humidity was raised stepwise to the highest value, measurements being made at each humidity. After the samples had been weighed at the highest humidity, the humidity was lowered stepwise to the lowest humidity, measurements again being made at each step. The acetates and stearates were humidified and measured in exactly the same manner as the acetylase, with the exception that only the absorption curve was determined and that measurements were made
only between 60 per cent and 95 per cent relative humidity. Thus, it was possible to compare the unesterified fibers and all the esterified materials at any humidity between 60 and 95 per cent. This was the humidity range wherein the differences between the various preparations were the largest and could be observed with the greatest ease. Samples of approximately 1 gram were cut from the conditioned handsheets, and were suspended by nichrome hooks in a humidity chamber (these hooks did not change weight at any of the humidities employed). The hygroscopicity determinations were made on the handsheets from the 0- and 40-minute intervals—i.e., corresponding to an unbeaten and a well-beaten material.

At least 48 hours were allowed to reach equilibrium in all cases; a somewhat longer time was necessary at the higher humidities. The weight at equilibrium was determined by shutting off the fan which circulated the air in the humidity chamber and making weighings of several samples. The fan was then started and allowed to run for a few hours, after which the samples were reweighed. If they were at constant weight, the whole set of samples were weighed and the saturated salt solution changed. After the final weighing under constant humidity conditions, the samples were removed from the cabinet and dried in the oven. The oven-dry weight of the cellulose was used for calculating the moisture content at the various relative humidities.

Salt solutions were used for controlling the humidity of the cabinet.
HYDROEXPANSIVITY MEASUREMENTS

The term "hydroexpansivity" may be defined as the property of a paper to expand or contract with a change in the relative humidity of the surrounding atmosphere. The methods of measuring the expansion and contraction of paper with a change in relative humidity have been reviewed by Van den Akker (22), who has developed a new method and apparatus for measuring the hydroexpansivity of paper. The original "Naanah Expansimeter" was designed to accommodate two test samples.

The new instrument developed by As the determination of hydroexpansivity is intrinsically slow, Van den Akker, Root, and Wink (23) constructed a new instrument by means of which 20 specimens can be measured simultaneously. The "Multiple-Specimen Naanah Expansimeter" was used throughout the present investigation. Hydroexpansivity measurements were made on papers prepared from the unacetylated material, the acetates, the butyrates, and the stearates, according to the procedure described below.

Duplicate strips, 1 inch wide and 5.5 inches long, were cut from the "British" hand sheets which had been conditioned as described above. These samples were clamped in the expansimeter with a clamp at the top and a T-shaped wire at the bottom. The T of the wire was dipped in melted rosin-beeswax and was applied to the specimen so that the stem of the link was centered and placed parallel with the strip. The specimens were so clamped that the measurements were made on a specimen exactly 5 inches long; thus, the change in length in inches, multiplied by 20, gave directly the percentage change in length or hydroexpansivity.
The procedure for conditioning the samples before the measurements were made was, first, to lower the humidity in the exsiccator (with the samples in place) from that of the room (50 per cent) to the lowest value to be used. Then, a complete cycle from the lowest to the highest humidity and back to the lowest humidity was made. The purpose of subjecting the samples to this cycle, before the readings were taken, was to minimize the effect of the past history of the samples. After the completion of the first cycle, measurements were taken at the lowest humidity and another complete cycle between the lowest and the highest humidity back to the lowest humidity was made. The humidity was raised and lowered by steps during the second cycle, and measurements of the changes in length of the samples and of the exact relative humidity were made at each point in the cycle. The varying temperature of the exsiccator during these measurements was a source of error which could not be eliminated.

The saturated salt solutions used for humidification purposes and the approximate humidities to be expected from the use of these solutions were: lithium chloride, 9-11 per cent; calcium chloride, 30-35 per cent; sodium nitrite, 60-65 per cent; and potassium chromate, 30-34 per cent.

In measurements of this type, a base point must be chosen for calculating the changes in length of the strips. In this investigation, the calculated changes in length were based upon the length of the sample at the lowest humidity of the second absorption cycle. Thus, the change in length is always given as the percentage change in length of the sheets between two humidities. On account of the difficulty of reproducing the same relative humidity with saturated salt solutions in consecutive experiments, the exact humidities were measured
each time and the original measurements of the percentage change in length were plotted against the relative humidity of the samples. The curves thus obtained were then interpolated to a common basis, so that all the results would be comparable.

EXPERIMENTAL DATA AND RESULTS

ACETATES

ACCELERATION OF THE ACETYLATION PROCESS

Effect of Temperature on the Rate of Acetylation and Degradation

The rate of acetylation, using pyridine and acetic anhydride at temperatures of 40°C or below, is exceedingly slow after the first few percent of acetyl have been introduced. The time required to attain an acetyl content of between 20 and 25 per cent (at these low temperatures) is usually over 30 days. Therefore, it was thought advisable to determine whether the rate of acetylation could be increased by increasing the temperature without, of course, degrading the cellulose. Hess and Ljubitsch (11), using the original acetylation procedure of steeping in strong alkali prior to acetylation, found that acetylation at elevated temperatures increased the rate of substitution but that little was gained when 50°C was exceeded. Blatzinger (1) found a substantial increase in the rate of acetylation on increasing the temperature from 24°C to about 40°C; the degree of polymerization of the cellulose, as determined by the Staudinger method, did not decrease appreciably during this accelerated esterification process.

The following experiments on the effect of temperature were carried out on small samples of pulp with the usual ratio of chemicals
to pulp. The methods of washing the ester were the same as in the standard procedure, so that the only variable involved was temperature. The results of this study, using a bleached Mitscherlich pulp, are given in Table II. It is seen that the rate of acetylation was increased considerably at a temperature higher than $35^\circ$ C.—i.e., the rates were greatly increased at $60^\circ$ C. and $30^\circ$ C. as compared with the results of acetylation at $40^\circ$ C., which is the temperature used by Blatzynger and by Aiken for preparing their higher acetylated samples and which was generally employed in this study. To illustrate the effect of temperature it may be mentioned that, whereas about 3 days were required to reach 15.87 per cent acetyl and 13 days to reach 18.1 per cent acetyl at $40^\circ$ C., approximately the same result (17.2 per cent acetyl) was accomplished in 1 day at $60^\circ$ C. At $30^\circ$ C., an even higher acetyl content (19.75 per cent acetyl) was reached in 24 hours. However, on longer contact at $30^\circ$ C., the rate of acetylation decreased; after 115 hours, an acetyl content of only 24.8 per cent was obtained.

In all acetylations, the reaction seemed to reach a point where further introduction of acetyl groups proceeded very slowly. The possibility of speeding up the reaction by removing the initial acetylation mixture and replacing it with a fresh acetylation bath was considered. A sample of pulp was placed in the acetylation mixture for 24 hours at $30^\circ$ C., after which the initial acetylation mixture was removed as completely as possible by suction on a Schlencker funnel, replaced with a fresh acetylation bath, and returned to the constant temperature bath at $60^\circ$ C. for another 24 hours. However, with these two 24-hour periods with fresh acetylation baths, or a total acetylation time of
### Table II

**EFFECT OF TIME AND TEMPERATURE ON ACETYLATION USING ACETIC ANHYDRIDE AND PYRIDINE**

<table>
<thead>
<tr>
<th>Pyridine, ml./g.</th>
<th>Acetic Anhydride, ml./g.</th>
<th>Temperature, °C</th>
<th>Time, hr.</th>
<th>Acetyl, %</th>
<th>D.P. Original Cellulose Basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>10</td>
<td>25</td>
<td>23</td>
<td>14.05</td>
<td>1653</td>
</tr>
<tr>
<td>16</td>
<td>10</td>
<td>25</td>
<td>0.5</td>
<td>17.14</td>
<td>1610</td>
</tr>
<tr>
<td>16</td>
<td>10</td>
<td>30</td>
<td>23.5</td>
<td>19.75</td>
<td>1675</td>
</tr>
<tr>
<td>16</td>
<td>10</td>
<td>30</td>
<td>115</td>
<td>25.8</td>
<td>1520</td>
</tr>
<tr>
<td>16</td>
<td>10</td>
<td>30</td>
<td>48**</td>
<td>22.3</td>
<td></td>
</tr>
</tbody>
</table>

* ml. per gram of cellulose.

** Acetylating bath replaced after first 24 hours by a fresh one of the same concentration.

After 48 hours, an acetyl content of only 22.3% per cent was obtained.

Table II also contains the degrees of polymerization of the various acetates. The values indicate that the extent to which the cellulose was degraded at the higher temperatures was negligible as long as these temperatures were not maintained for too long a period of time. The prolonged treatment of 115 hours at 30° C. caused some degradation (about 3 per cent). However, this slight decrease in the degree of polymerization should have very little effect upon the strength properties of a sheet because, according to Staudinger and Jurisch (24), the amount of degradation does not affect the strength of native cellulose until the molecular weight falls below about 160,000 or a degree of polymerization of about 1000.
From this study of the rate of acetylation and the extent to which degradation occurred at higher temperatures, it appears that a higher temperature could be used without harm if it were necessary to accelerate the acetylation process for the preparation of acetates containing up to about 25 per cent acetyl.

Acetylation with Acetyl Chloride

Experiments were carried out to determine the rate of acetylation and the extent of degradation of cellulose when acetyl chloride was the esterifying agent. These experiments were undertaken to ascertain whether the acid chloride could be used in cases where difficulties were encountered in introducing a sufficient quantity of the radical by the anhydride-pyridine method.

The use of acetyl chloride in the presence of pyridine was first suggested by Kohl (25), who prepared a soluble tricarbonate by adding to the mixture a solvent for the tricarbonate (nitrobenzene). Thilo (26) prepared a fibrous acetate by refluxing cellulose fibers for 17 hours with an acetylation mixture of acetyl chloride, pyridine, and a nonsolvent diluent (benzene).

In the present investigation, a method similar to that employed by Thilo was used; the conditions were milder, because the purpose in this study was to obtain a fibrous acetate as little degraded as possible. Thus, the ratio of chemicals to cellulose and the temperatures were kept at lower levels. To obtain varying degrees of substitution, the molar ratio of acetyl chloride to cellulose was changed; the total volume of the acetylation mixture and the ratio of the acetyl
chloride to pyridine were held constant. Likewise, the temperature and time were kept constant at 35°C and 24 hours, respectively.

The procedure used in the acetylations was as follows: The pulp sample was allowed to swell in pyridine overnight. The excess pyridine was removed on a Büchner funnel, and the pulp pad was weighed. The calculated amount of acetylation mixture was made up, allowing for the pyridine in the pad, and the temperature of the solution was determined. The acetylation mixture was then added to the pulp pad while the mass was stirred vigorously. After the pulp and the acetylation mixture had been thoroughly mixed, the charges were set aside for 24 hours. At the end of the 24 hours, the acetylation mixture was filtered on a Büchner funnel. The acetylated pulp was then washed twice with hot benzene, twice with chloroform, three times with ethanol, and finally three times with ether. After the last ether wash, it was sucked free of ether on a Büchner funnel and allowed to dry in the air.

The results of these experiments are given in Table III. From the values shown, it would appear that the rate of acetylation is dependent upon the molar ratio of acetyl chloride to cellulose, although the difference between the rates obtained with a molar ratio of 3:1 and a molar ratio of 5:1 is relatively small.

The data of Table III also indicate that the acetylations with acetyl chloride resulted in greater degradation of the pulp than occurred with acetic anhydride under the same conditions, and it would appear that this degradation increased with the degree of substitution. That the acetylation with acetyl chloride took place at a somewhat
TABLE III

ESTERIFICATION OF BEAKED PITCHCORK PULP WITH ACETYL CHLORIDE

<table>
<thead>
<tr>
<th>Mole Ratio of Cellulose to Acetyl Chloride</th>
<th>Acetyl Chloride, g./g. pulp</th>
<th>Pyridine, ml./g. pulp</th>
<th>Benzene, ml./g. pulp</th>
<th>Time, hr.</th>
<th>Temperature, °C.</th>
<th>Acetyl, %</th>
<th>D.P.*</th>
<th>Cellulose Basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original pulp</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1653</td>
</tr>
<tr>
<td>1:2</td>
<td>0.372</td>
<td>6.6</td>
<td>33.4</td>
<td>24</td>
<td>24</td>
<td>13.8</td>
<td>1510</td>
<td></td>
</tr>
<tr>
<td>1:1.4</td>
<td>1.652</td>
<td>11.5</td>
<td>37.0</td>
<td>24</td>
<td>24</td>
<td>17.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:5</td>
<td>2.424</td>
<td>16.9</td>
<td>34.4</td>
<td>24</td>
<td>24</td>
<td>13.1</td>
<td>1483</td>
<td></td>
</tr>
</tbody>
</table>

* Degree of polymerization on original cellulose basis.
faster rate than with acetic anhydride is seen from the following comparison: At 30° C., 24 hours were required to produce an acetyl content of 15.27 per cent with acetic anhydride, whereas only 24 hours were required to produce an even higher acetyl content (17.45 per cent) when using acetyl chloride (mole ratio of 3.4:1) at the same temperature. However, when the temperature during acetylation with acetic anhydride was increased to 60° C., the time (as has been shown) required to produce an acetyl content of 17.1 per cent could be decreased to 24 hours. In addition, the product thus obtained suffered no decrease in the degree of polymerization. There appears to be no advantage in using the acid chloride method instead of the anhydride method in the preparation of practically undegraded fibrous cellulose acetates. If, however, degradation is not of primary importance and a high degree of substitution is desired, the acid chloride method is preferable. It may be mentioned that the present direct comparison between the two methods seems to be the first one recorded.

PHYSICAL STRENGTH PROPERTIES OF UNACETYLATED AND ACETYLATED HITSCHERLICH PULPS WHEN PROCESSED IN WATER

In order to secure data on the physical properties of the unacetylated and the acetylated Mitscherlich pulps, handsheets were made up at 0, 20, 40, and 60-minute beating intervals, according to standard procedures, and the physical strength properties were determined. A summary of the results is given in Table IV. Table IVA shows the results calculated on the basis of cellulose.
### Table IV

**Physical Strength Properties of Acetylated Poplars High pulp of Increasing Acetyl Content at Various Beating Times**

#### Unacetylated Raw Material

<table>
<thead>
<tr>
<th>Beating time, min.</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>40</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basis weight, lb.</td>
<td>43.4</td>
<td>43.5</td>
<td>43.5</td>
<td>43.5</td>
<td>43.3</td>
</tr>
<tr>
<td>Caliper, mils</td>
<td>4.28</td>
<td>2.98</td>
<td>2.8</td>
<td>2.66</td>
<td>2.62</td>
</tr>
<tr>
<td>Apparent density</td>
<td>10.1</td>
<td>14.6</td>
<td>15.5</td>
<td>16.3</td>
<td>16.5</td>
</tr>
<tr>
<td>Burst factor</td>
<td>26.2</td>
<td>13.4</td>
<td>156.0</td>
<td>161.5</td>
<td>162.0</td>
</tr>
<tr>
<td>Tear factor</td>
<td>2.63</td>
<td>0.11</td>
<td>0.995</td>
<td>0.29</td>
<td>0.265</td>
</tr>
<tr>
<td>Tensile factor</td>
<td>11.7</td>
<td>40.0</td>
<td>48.5</td>
<td>51.4</td>
<td>50.4</td>
</tr>
</tbody>
</table>

#### 2.6% Acetyl - 3.7% Hydroxyl Groups Covered

<table>
<thead>
<tr>
<th>Beating time, min.</th>
<th>0</th>
<th>20</th>
<th>40</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basis weight, lb.</td>
<td>43.4</td>
<td>43.2</td>
<td>42.5</td>
<td>42.4</td>
</tr>
<tr>
<td>Caliper, mils</td>
<td>4.16</td>
<td>2.96</td>
<td>2.82</td>
<td>2.56</td>
</tr>
<tr>
<td>Apparent density</td>
<td>10.4</td>
<td>14.6</td>
<td>16.1</td>
<td>16.5</td>
</tr>
<tr>
<td>Burst factor</td>
<td>32.5</td>
<td>17.6</td>
<td>183</td>
<td>186</td>
</tr>
<tr>
<td>Tear factor</td>
<td>2.66</td>
<td>0.925</td>
<td>0.825</td>
<td>0.787</td>
</tr>
<tr>
<td>Tensile factor</td>
<td>12.6</td>
<td>54.9</td>
<td>55.8</td>
<td>55.1</td>
</tr>
</tbody>
</table>

#### 4.6% Acetyl - 7.1% Hydroxyl Groups Covered

<table>
<thead>
<tr>
<th>Beating time, min.</th>
<th>0</th>
<th>20</th>
<th>40</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basis weight, lb.</td>
<td>42.9</td>
<td>43.1</td>
<td>42.9</td>
<td>42.9</td>
</tr>
<tr>
<td>Caliper, mils</td>
<td>3.9</td>
<td>2.74</td>
<td>2.56</td>
<td>2.56</td>
</tr>
<tr>
<td>Apparent density</td>
<td>10.6</td>
<td>15.9</td>
<td>16.5</td>
<td>16.5</td>
</tr>
<tr>
<td>Burst factor</td>
<td>34.8</td>
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<td>187</td>
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<tr>
<td>Tear factor</td>
<td>2.77</td>
<td>0.84</td>
<td>0.785</td>
<td>0.795</td>
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<tr>
<td>Tensile factor</td>
<td>12.4</td>
<td>17.4</td>
<td>53.5</td>
<td>54.4</td>
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</table>

#### 5.6% Acetyl - 6.1% Hydroxyl Groups Covered

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<tbody>
<tr>
<td>Basis weight, lb.</td>
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<td>43.1</td>
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<tr>
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<td>173</td>
<td>180</td>
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<tr>
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<td>0.792</td>
<td>0.797</td>
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<td>57.7</td>
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#### 5.8% Acetyl - 7.32% Hydroxyl Groups Covered

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<td>Basis weight, lb.</td>
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<td>42.6</td>
<td>42.6</td>
</tr>
<tr>
<td>Caliper, mils</td>
<td>4.13</td>
<td>2.80</td>
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</tr>
<tr>
<td>Apparent density</td>
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<td>15.4</td>
<td>16.2</td>
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<td>Burst factor</td>
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<td>0.355</td>
<td>0.95</td>
<td>0.767</td>
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<tr>
<td>Tensile factor</td>
<td>14.3</td>
<td>57.3</td>
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### TABLE IV (Continued)

#### 3.9\% Acetyl – 12.2\% Hydroxyl Groups Covered

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</thead>
<tbody>
<tr>
<td>Basis weight, lb.</td>
<td>38.3</td>
<td>43.1</td>
<td>43.3</td>
<td>42.9</td>
</tr>
<tr>
<td>Caliper, mils</td>
<td>4.2</td>
<td>2.76</td>
<td>2.62</td>
<td>2.58</td>
</tr>
<tr>
<td>Apparent density</td>
<td>9.35</td>
<td>15.25</td>
<td>16.7</td>
<td>16.55</td>
</tr>
<tr>
<td>Burst factor</td>
<td>32.8</td>
<td>143.6/143.8</td>
<td>138.6/143.4</td>
<td>143.4</td>
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<tr>
<td>Tear factor</td>
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<td>0.76</td>
<td>0.707</td>
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<td>46.7/</td>
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<td>50.8/</td>
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#### 10.05\% Acetyl – 14.0\% Hydroxyl Groups Covered

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</thead>
<tbody>
<tr>
<td>Basis weight, lb.</td>
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<td>43.1</td>
<td>43.3</td>
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<td>Caliper, mils</td>
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<tr>
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<td>16.2</td>
<td>16.4</td>
</tr>
<tr>
<td>Burst factor</td>
<td>25.2</td>
<td>138.2</td>
<td>142.2</td>
<td>149.6/150.6</td>
</tr>
<tr>
<td>Tear factor</td>
<td>2.17</td>
<td>0.822</td>
<td>0.815</td>
<td>0.765</td>
</tr>
<tr>
<td>Tensile factor</td>
<td>10.4/</td>
<td>46.9/</td>
<td>49.7/</td>
<td>53.7/</td>
</tr>
</tbody>
</table>

#### 10.6\% Acetyl – 14.3\% Hydroxyl Groups Covered

<table>
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</thead>
<tbody>
<tr>
<td>Basis weight, lb.</td>
<td>38.5</td>
<td>43.1</td>
<td>43.3</td>
<td>42.9</td>
</tr>
<tr>
<td>Caliper, mils</td>
<td>3.6</td>
<td>2.76</td>
<td>2.6</td>
<td>2.5</td>
</tr>
<tr>
<td>Apparent density</td>
<td>10.7</td>
<td>15.6</td>
<td>16.3</td>
<td>17.0</td>
</tr>
<tr>
<td>Burst factor</td>
<td>32.0</td>
<td>143.0</td>
<td>153.0/154.0</td>
<td>143.0/144.4</td>
</tr>
<tr>
<td>Tear factor</td>
<td>2.7</td>
<td>0.84</td>
<td>0.765</td>
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<td>12.75</td>
<td>49.6</td>
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</table>

#### 12.57\% Acetyl – 13.0\% Hydroxyl Groups Covered

<table>
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</thead>
<tbody>
<tr>
<td>Basis weight, lb.</td>
<td>42.1</td>
<td>41.3</td>
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<td>42.6</td>
</tr>
<tr>
<td>Caliper, mils</td>
<td>4.3</td>
<td>2.76</td>
<td>2.66</td>
<td>2.62</td>
</tr>
<tr>
<td>Apparent density</td>
<td>9.79</td>
<td>15.18</td>
<td>16.16</td>
<td>16.26</td>
</tr>
<tr>
<td>Burst factor</td>
<td>22.7</td>
<td>131.7</td>
<td>123.6/126</td>
<td>134.7/135.5</td>
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<tr>
<td>Tear factor</td>
<td>1.945</td>
<td>0.364</td>
<td>0.761</td>
<td>0.744</td>
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<td>48.9</td>
<td>49.9/50</td>
<td>48.8/48.9</td>
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#### 14.5\% Acetyl – 21.2\% Hydroxyl Groups Covered

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<th>60</th>
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</thead>
<tbody>
<tr>
<td>Basis weight, lb.</td>
<td>33.9</td>
<td>18.3</td>
<td>17.6</td>
<td>17.4</td>
</tr>
<tr>
<td>Caliper, mils</td>
<td>4.5</td>
<td>2.74</td>
<td>2.62</td>
<td>2.5</td>
</tr>
<tr>
<td>Apparent density</td>
<td>9.76</td>
<td>15.4</td>
<td>16.25</td>
<td>16.25</td>
</tr>
<tr>
<td>Burst factor</td>
<td>15.7</td>
<td>131.7</td>
<td>127</td>
<td>128.2</td>
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<tr>
<td>Tear factor</td>
<td>1.63</td>
<td>0.93</td>
<td>0.804</td>
<td>0.794</td>
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<td>7.66</td>
<td>46.2</td>
<td>48.8</td>
<td>48.9/48.8</td>
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### Table IV (Continued)

#### 15.57% Acetyl - 71.6% Hydroxyl Groups Covered

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</thead>
<tbody>
<tr>
<td>Basis weight, lb.</td>
<td>43.7</td>
<td>42.3</td>
<td>41.9</td>
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</tr>
<tr>
<td>Collier, mile</td>
<td>5.32</td>
<td>5.08</td>
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<tr>
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<td>14.0</td>
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<td>17.2</td>
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#### 18.1% Acetyl - 67.5% Hydroxyl Groups Covered

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</thead>
<tbody>
<tr>
<td>Basis weight, lb.</td>
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</tr>
<tr>
<td>Collier, mile</td>
<td>5.46</td>
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<td>5.08</td>
<td>5.02</td>
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<td>7.77</td>
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<td>13.6</td>
<td>14.1</td>
</tr>
<tr>
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<td>47.7</td>
<td>59.5</td>
<td>51.7</td>
</tr>
<tr>
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<td>1.053</td>
<td>0.938</td>
<td>0.603</td>
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<td>Tensile factor</td>
<td>4.79</td>
<td>14.46</td>
<td>15.4</td>
<td>16.8</td>
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</table>

#### 20.1% Acetyl - 71.4% Hydroxyl Groups Covered

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<th>40</th>
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</thead>
<tbody>
<tr>
<td>Basis weight, lb.</td>
<td>42.2</td>
<td>40.3</td>
<td>40.7</td>
</tr>
<tr>
<td>Collier, mile</td>
<td>5.5</td>
<td>4.96</td>
<td>4.02</td>
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<td>Apparent density</td>
<td>7.67</td>
<td>12.86</td>
<td>25.6</td>
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<tr>
<td>Burst factor</td>
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<td>3.459</td>
<td>14.7</td>
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<tr>
<td>Tear factor</td>
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<td>2.66</td>
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<tr>
<td>Tensile factor</td>
<td>4.26-4</td>
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#### 23.5% Acetyl - 43% Hydroxyl Groups Covered

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</tr>
</thead>
<tbody>
<tr>
<td>Basis weight, lb.</td>
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<td>42.6</td>
<td>42.6</td>
<td>42.6</td>
</tr>
<tr>
<td>Collier, mile</td>
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<td>6.7</td>
<td>6.7</td>
<td>6.7</td>
</tr>
<tr>
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<td>6.71</td>
<td>6.71</td>
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<tr>
<td>Burst factor</td>
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<td>3.76-5</td>
<td>3.76-5</td>
<td>3.76-5</td>
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<td>0.75</td>
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<td>4.76</td>
<td>4.76</td>
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<td>Table IVa</td>
<td>Physical Strength Properties of Acetylated Pitch Charcoal Pulps (Table IV) Calculated on Original Cellulose Basis</td>
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<tr>
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<tr>
<td>Unacetylated Raw Material</td>
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<td>Beating time, min.</td>
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<td>40</td>
<td>60</td>
</tr>
<tr>
<td>Basis weight, lb.</td>
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<td>43.5</td>
<td>43.5</td>
<td>43.3</td>
</tr>
<tr>
<td>Caliper, mils</td>
<td>4.25</td>
<td>2.98</td>
<td>2.86</td>
<td>2.66</td>
</tr>
<tr>
<td>Apparent density</td>
<td>14.1</td>
<td>14.6</td>
<td>15.5</td>
<td>16.3</td>
</tr>
<tr>
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<td>26.2</td>
<td>134.2</td>
<td>136.0</td>
<td>161.0</td>
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<tr>
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<td>2.68</td>
<td>1.1</td>
<td>0.995</td>
<td>0.39</td>
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<tr>
<td>Tensile factor</td>
<td>11.2</td>
<td>40.0</td>
<td>48.5</td>
<td>51.1</td>
</tr>
</tbody>
</table>

2.52% Acetyl - 3.2% Hydroxyl Groups Covered

| Beating time, min. | 0 | 20 | 40 | 60 |
| Basis weight, lb. | 42.3 | 42.1 | 41.3 | 41.4 |
| Caliper, mils | 4.16 | 2.96 | 2.62 | 2.56 |
| Apparent density | 14.1 | 14.1 | 16.7 | 16.1 |
| Burst factor | 33.1 | 176.2 | 190.6 | 191.1 |
| Tear factor | 2.73 | 0.342 | 0.846 | 3.86 |
| Tensile factor | 12.5 | 57.3 | 57.6 | 56.5 |

2.64% Acetyl - 3.4% Hydroxyl Groups Covered

| Beating time, min. | 0 | 20 | 40 | 60 |
| Basis weight, lb. | 42.2 | 42.1 | 42.4 | 41.2 |
| Caliper, mils | 4.06 | 2.72 | 2.58 | 2.53 |
| Apparent density | 14.3 | 15.5 | 16.1 | 16.4 |
| Burst factor | 39.5 | 181.7 | 183.9 | 192 |
| Tear factor | 2.84 | 0.38 | 0.806 | 2.72 |
| Tensile factor | 12.7 | 53.9 | 54.9 | 55.8 |

4.65% Acetyl - 6.1% Hydroxyl Groups Covered

| Beating time, min. | 0 | 20 | 40 | 60 |
| Basis weight, lb. | 41.0 | 41.2 | 41.0 | 41.1 |
| Caliper, mils | 3.9 | 3.74 | 2.6 | 2.6 |
| Apparent density | 10.5 | 15.0 | 15.76 | 15.85 |
| Burst factor | 19.0 | 178.5 | 186.5 | 133.9 |
| Tear factor | 2.31 | 0.842 | 0.829 | 0.803 |
| Tensile factor | 17.9 | 59.9 | 58.2 | 64.0 |

5.67% Acetyl - 7.8% Hydroxyl Groups Covered

| Beating time, min. | 0 | 20 | 40 | 60 |
| Basis weight, lb. | 40.5 | 40.5 | 40.2 | 40.1 |
| Caliper, mils | 4.13 | 2.80 | 2.63 | 2.58 |
| Apparent density | 10.0 | 14.5 | 15.3 | 15.6 |
| Burst factor | 37.3 | 176 | 131.4 | 137.4 |
| Tear factor | 2.80 | 0.917 | 0.901 | 0.814 |
| Tensile factor | 14.7 | 53.4 | 60.4 | 51.1 |
TABLE IV (Continued)

2.95 Acetyl - 14.3% Hydroxyl Groups Covered

<table>
<thead>
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<th>Beating time, min</th>
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<th>20</th>
<th>40</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basis weight, lb.</td>
<td>35.2</td>
<td>35.4</td>
<td>40.0</td>
<td>39.7</td>
</tr>
<tr>
<td>Caliper, mils</td>
<td>4.3</td>
<td>4.76</td>
<td>4.64</td>
<td>4.58</td>
</tr>
<tr>
<td>Apparent density</td>
<td>9.03</td>
<td>13.52</td>
<td>15.26</td>
<td>15.1</td>
</tr>
<tr>
<td>Burst factor</td>
<td>35.4</td>
<td>153</td>
<td>173.7</td>
<td>159</td>
</tr>
<tr>
<td>Tear factor</td>
<td>2.94</td>
<td>1.0</td>
<td>0.833</td>
<td>0.84</td>
</tr>
<tr>
<td>Tensile factor</td>
<td>11.31</td>
<td>51.1</td>
<td>62.5</td>
<td>55.6</td>
</tr>
</tbody>
</table>

10.05% Acetyl - 14.5% Hydroxyl Groups Covered

<table>
<thead>
<tr>
<th>Beating time, min</th>
<th>0</th>
<th>20</th>
<th>40</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basis weight, lb.</td>
<td>42.1</td>
<td>37.9</td>
<td>38.3</td>
<td>38.2</td>
</tr>
<tr>
<td>Caliper, mils</td>
<td>4.53</td>
<td>2.84</td>
<td>2.64</td>
<td>2.58</td>
</tr>
<tr>
<td>Apparent density</td>
<td>9.2</td>
<td>14.3</td>
<td>14.6</td>
<td>14.5</td>
</tr>
<tr>
<td>Burst factor</td>
<td>38.3</td>
<td>153.5</td>
<td>157.2</td>
<td>165.9</td>
</tr>
<tr>
<td>Tear factor</td>
<td>2.41</td>
<td>0.99</td>
<td>0.904</td>
<td>0.848</td>
</tr>
<tr>
<td>Tensile factor</td>
<td>11.7</td>
<td>52.0</td>
<td>54.0</td>
<td>53.9</td>
</tr>
</tbody>
</table>

10.65% Acetyl - 14.8% Hydroxyl Groups Covered

<table>
<thead>
<tr>
<th>Beating time, min</th>
<th>0</th>
<th>20</th>
<th>40</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basis weight, lb.</td>
<td>34.5</td>
<td>33.6</td>
<td>37.7</td>
<td>38.2</td>
</tr>
<tr>
<td>Caliper, mils</td>
<td>3.6</td>
<td>2.76</td>
<td>2.6</td>
<td>2.5</td>
</tr>
<tr>
<td>Apparent density</td>
<td>9.6</td>
<td>14.0</td>
<td>14.5</td>
<td>14.2</td>
</tr>
<tr>
<td>Burst factor</td>
<td>35.3</td>
<td>160</td>
<td>171.6</td>
<td>160.3</td>
</tr>
<tr>
<td>Tear factor</td>
<td>3.1</td>
<td>0.133</td>
<td>0.894</td>
<td>0.797</td>
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<tr>
<td>Tensile factor</td>
<td>14.2</td>
<td>58.7</td>
<td>57.4</td>
<td>58.2</td>
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</tbody>
</table>

12.57% Acetyl - 13.9% Hydroxyl Groups Covered

<table>
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<tr>
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<th>20</th>
<th>40</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basis weight, lb.</td>
<td>37.0</td>
<td>36.8</td>
<td>37.3</td>
<td>37.4</td>
</tr>
<tr>
<td>Caliper, mils</td>
<td>4.3</td>
<td>2.76</td>
<td>2.66</td>
<td>2.62</td>
</tr>
<tr>
<td>Apparent density</td>
<td>9.6</td>
<td>13.34</td>
<td>14.2</td>
<td>14.3</td>
</tr>
<tr>
<td>Burst factor</td>
<td>35.3</td>
<td>140.4</td>
<td>147.5</td>
<td>153.4</td>
</tr>
<tr>
<td>Tear factor</td>
<td>2.22</td>
<td>0.484</td>
<td>0.89</td>
<td>0.848</td>
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<tr>
<td>Tensile factor</td>
<td>10.5</td>
<td>55.2</td>
<td>56.8</td>
<td>55.6</td>
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</tbody>
</table>

14.5% Acetyl - 21.2% Hydroxyl Groups Covered

<table>
<thead>
<tr>
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<th>20</th>
<th>40</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basis weight, lb.</td>
<td>37.7</td>
<td>36.3</td>
<td>36.6</td>
<td>35.4</td>
</tr>
<tr>
<td>Caliper, mils</td>
<td>4.55</td>
<td>3.76</td>
<td>3.62</td>
<td>3.5</td>
</tr>
<tr>
<td>Apparent density</td>
<td>8.32</td>
<td>13.72</td>
<td>13.95</td>
<td>14.35</td>
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<tr>
<td>Burst factor</td>
<td>22.2</td>
<td>141.7</td>
<td>143</td>
<td>149.6</td>
</tr>
<tr>
<td>Tear factor</td>
<td>1.36</td>
<td>1.25</td>
<td>0.936</td>
<td>0.828</td>
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<tr>
<td>Tensile factor</td>
<td>5.32</td>
<td>5.37</td>
<td>56.3</td>
<td>56.6</td>
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</table>
### TABLE IVA (Continued)

#### 15.87% Acetyl - 23.6% Hydroxyl Groups Covered

<table>
<thead>
<tr>
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<th>60</th>
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</thead>
<tbody>
<tr>
<td>Basis weight, lb.</td>
<td>36.9</td>
<td>35.7</td>
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<td>Caliper, mils</td>
<td>4.84</td>
<td>3.02</td>
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<tr>
<td>Apparent density</td>
<td>7.65</td>
<td>11.8</td>
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<td>13.7</td>
</tr>
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<td>Burst factor</td>
<td>16.3</td>
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<td>87.7</td>
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<tr>
<td>Tear factor</td>
<td>1.32</td>
<td>1.34</td>
<td>1.17</td>
<td>0.96</td>
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<tr>
<td>Tensile factor</td>
<td>4.29</td>
<td>32.9</td>
<td>40.1</td>
<td>42.7</td>
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</table>

#### 22.1% Acetyl - 27.6% Hydroxyl Groups Covered

<table>
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<tr>
<th>Beating time, min.</th>
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<th>20</th>
<th>40</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basis weight, lb.</td>
<td>34.5</td>
<td>34.5</td>
<td>34.6</td>
<td>35.6</td>
</tr>
<tr>
<td>Caliper, mils</td>
<td>5.42</td>
<td>3.39</td>
<td>3.00</td>
<td>3.02</td>
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<tr>
<td>Apparent density</td>
<td>5.44</td>
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<td>10.7</td>
<td>11.6</td>
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<td>Burst factor</td>
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<td>33.7</td>
<td>38.6</td>
<td>40.6</td>
</tr>
<tr>
<td>Tear factor</td>
<td>1.32</td>
<td>1.23</td>
<td>0.86</td>
<td>0.733</td>
</tr>
<tr>
<td>Tensile factor</td>
<td>5.06</td>
<td>17.95</td>
<td>19.7</td>
<td>20.8</td>
</tr>
</tbody>
</table>

#### 20.1% Acetyl - 31.1% Hydroxyl Groups Covered

<table>
<thead>
<tr>
<th>Beating time, min.</th>
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<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basis weight, lb.</td>
<td>34</td>
<td>34</td>
</tr>
<tr>
<td>Caliper, mils</td>
<td>5.5</td>
<td>3.28</td>
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<tr>
<td>Apparent density</td>
<td>6.13</td>
<td>10.35</td>
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<tr>
<td>Burst factor</td>
<td>11.8</td>
<td>31.00</td>
</tr>
<tr>
<td>Tear factor</td>
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<td>0.819</td>
</tr>
<tr>
<td>Tensile factor</td>
<td>4.92</td>
<td>17.9</td>
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</tbody>
</table>

#### 25.65% Acetyl - 43% Hydroxyl Groups Covered

<table>
<thead>
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<th>Beating time, min.</th>
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<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basis weight, lb.</td>
<td>32.7</td>
<td>31.5</td>
</tr>
<tr>
<td>Caliper, mils</td>
<td>5.7</td>
<td>4.3</td>
</tr>
<tr>
<td>Apparent density</td>
<td>4.37</td>
<td>7.32</td>
</tr>
<tr>
<td>Burst factor</td>
<td>6.1</td>
<td>6.94</td>
</tr>
<tr>
<td>Tear factor</td>
<td>0.407</td>
<td>0.94</td>
</tr>
<tr>
<td>Tensile factor</td>
<td>2.15</td>
<td>3.07</td>
</tr>
</tbody>
</table>
The data show that the strength properties of the acetylated Hitzschelrich pulps followed the same general trend observed by Blatzinger and Aiken in their work using rag stocks and Hitzschelrich pulp. There was an initial increase in bursting and tensile strengths with the introduction of a small percentage of acetyl. As the degree of acetylation increased and the hydrophilic properties decreased, the strength properties fell rapidly until, at 25.65 per cent acetyl content, the minimum strength values were reached. The changes were less pronounced with the tearing strength.

Figures 1 (zero interval) and 2 (40-minute beating interval) show that the maximum bursting and tensile strength increases were attained by the acetylated materials when their acetyl content was between 2 and 3 per cent; their strength properties were also above those of the original material until about 10 per cent acetyl content was reached. The maxima in strength properties with increasing acetyl content were shown by both the unbeaten and beaten materials. The maximum was more pronounced with the beaten material.

As mentioned above, the acetylated fibers become more and more hydrophobic as the degree of substitution was increased. Likewise, they were more difficult to break up and thoroughly disperse. However, no trouble was encountered from fibers clumping together, if the standard procedure of disintegration was followed. The difficulties encountered by Blatzinger and Aiken were probably due to a lack of thorough disintegration. On the other hand, it was observed that, after beating, the fibers with the higher acetyl content (25.65 per cent) tended to

Continue...
FIGURE 1

PHYSICAL STRENGTH PROPERTIES
OF ACETYLATED PULPS

ZERO BEATING INTERVAL

Curve 1  Tearing Strength
Curve 2  Tensile Strength
Curve 3  Bursting Strength

Tensile Strength (lb./100 lb.)

Burst Factor (lb./sq. in. per 100 lb.)

0  10  20  30  40
(0) (7.5) (14) (19.5) (24.4)

Percentage of Hydroxyl Groups Replaced by Acyl Groups
(Percentage of acyl by weight in brackets)
FIGURE 2

PHYSICAL STRENGTH PROPERTIES
OF ACETYLATED PULPS

40-MINUTE BEATING INTERVAL

Curve 1  Tearing Strength
Curve 2  Tensile Strength
Curve 3  Bursting Strength

Y-axis: Burst Factor (lb./min. per 100 lb.)
X-axis: Percentage of Hydroxyl Groups Replaced by Acyl Groups
(Percentage of acyl by weight in brackets)
have become powdery and to have been broken rather than fibrillated. They also showed an increased breakage. Furthermore, the end did not brush-out on beating but remained more or less blunt. On the other hand, the unacetylated pulp and the lower acetylated fibers showed the fibrillation and brushing-out on beating normally observed. Photomicrographs of the unacetylated pulp, unbeaten and beaten for 40 minutes in the Lempen mill, as well as of the pulp containing 25.65% acetyl, beaten for 40 minutes in the Lempen mill, are shown in Figures 3, 4, and 5. These photomicrographs were taken with dark field illumination at 200 magnifications.

The fact that the fibers break and have a tendency to fibrillate probably explains, in part, the lack of strength development observed when the pulps with the higher acetyl contents are beaten in water. The results presented above suggest that the hypothesis advanced earlier and outlined in the beginning of the paper holds.

The results of the evaluation of the physical strength properties of the acetylated pulps support the hypothesis which was suggested earlier to explain their behavior when brought into contact with water. The introduction of a small amount of acetyl is assumed to open up the internal structure of the fiber so that more hydroxyl groups become accessible to water, thus favoring hydration and subsequent bonding between adjacent fibers. However, on further increase of the acetyl content, the hydrophobic character of the fibers becomes more and more predominant; this inhibits hydration and subsequent bonding. As a result, the physical strength properties decrease. This loss of physical strength properties seems to be caused, in part, by the breaking of the acetylated fibers when they are subjected to
Figure 3

Unacetylated Mitscherlich Pulp
(Zero Interval)
Position 6
Figure 4

Unacetylated Mitscherlich Pulp
(40 Minute Interval)
Figure 5

Acetylated Pulp - Processed in Water
25.65% Acetyl Content
(40 Minute Interval)
mechanical agitation.

In addition, it is seen from the "zero-beating time" values in Tables IV and IVA that the phenomenon of strength development to a maximum (and its subsequent decrease) occurs with the unbeaten fibers. This was observed also by Aiken. The slightly acetylated fibers require no actual beating to reveal the changes which have taken place. It would appear that the opening of the micellar structure of the fibers, on the introduction of acetyl groups, suffices to produce the increased physical strength when a sheet of paper is prepared from acetylated fibers which have received only a minimum of mechanical agitation.

THE HYGROSCOPICITY OF THE ACETYLATED PULPS AND ITS RELATION TO THEIR PHYSICAL STRENGTH PROPERTIES

Aiken (2) showed that a direct relation existed between the water-binding capacity, the physical strength properties, and the acetyl content of acetylated rag stocks. If the maximum in physical strength properties is a result of maximum hydration, it should coincide with a maximum in hygroscopicity of the fibers of limited acetyl content. In working with acetylated Mitscherlich pulps, Aiken determined the hygroscopicity of the unbeaten material at one point only—namely, at 91.2 per cent relative humidity. He found no appreciable change in the water-binding properties of the acetylated materials up to about 4 per cent acetyl content; beyond that value, the amount of moisture retained diminished with increasing acetyl content.
In the present investigation, the study of this relationship was extended to acetylated Mitscherlich pulps in both the un-
beaten and the beaten state and at various humidities. Tables V and VI show the hygroscopicities of the unacetylated and the acetylated
Mitscherlich pulps at increasing and decreasing humidities. The measurements were made on samples taken from the zero and 40-minute
beating intervals, which are designated simply as "unbeaten" and "beaten" pulps. From the actual data obtained experimentally, hysteresis curves
for the various pulps were plotted and interpolated to give the per-
centage moisture content at humidities of 70, 40, 60, 30, and 20 per
cent. The data thus obtained are shown in Tables V and VI. The
changes were most distinct at 90 per cent relative humidity; therefore,
the data at this humidity were used for the evaluation.

These data are also shown in Figures 6 and 7. The middle
columns along the ordinates show the moisture contents at 90 per cent
relative humidity, and the figures on the abscissae represent the
percentage of hydroxyl groups replaced and, in brackets, the acetyl
content of the samples. They may be interpreted as follows: The
moisture contents of both the unbeaten and the beaten samples increased
with the introduction of small amounts of acetyl, which was followed
by a rather rapid decrease as more hydroxyl groups were replaced. In
general, the beaten stock appears to have a slightly higher moisture
content at any given acetyl content. However, with the exception of
the products with 13.1 and the 23.65 per cent of acetyl, the differ-
ences were within the experimental error of the procedure. For these
two materials, the differences were greater; an effect, such as the
<table>
<thead>
<tr>
<th>Acetyl Content, %</th>
<th>0% R. H.</th>
<th>40% R. H.</th>
<th>Percentage Moisture Content at Various Humidities</th>
</tr>
</thead>
<tbody>
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<td>Raw Material</td>
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<td>40-min.</td>
<td>0</td>
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<td>10.5</td>
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<td>5.3</td>
<td>8.8</td>
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<tr>
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<td>1.8</td>
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<td>3.1</td>
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</table>

+ Zero interval or unbeaten pulp

++ 40-minute beating interval
### Table VI

**Sheets made from**

<table>
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<th>20% R.H.</th>
<th>40°-50°</th>
<th>60°-70°</th>
<th>80-90°</th>
<th>0% R.H.</th>
<th>10°-20°</th>
<th>20°-30°</th>
<th>30°-40°</th>
<th>40°-50°</th>
<th>50°-60°</th>
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<th>70°-80°</th>
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<td>25.7</td>
<td>27.7</td>
<td>29.7</td>
</tr>
</tbody>
</table>

+ Zero interval or unheated pulp.

+ 10-minute heating interval.
FIGURE 6

Comparing the physical properties with the physical properties of the treated samples and the control samples. The treated and control samples were subjected to different heating intervals.

Curve 1: Bursting Strength
Curve 2: Hygroscopicity
Curve 3: Hygroexpansivity

Percentage Change in Length (Humidity Change: 10% to 60%)

Percentage Moisture Content (50% Relative Humidity)

Bursting Strength (lb./sq. in. per 100 lb.)

Percentage of Hydroxyl Groups Replaced by Acyl Groups

(Percentage of acyl by weight in brackets)
FIGURE 7

COMPARISON OF THE PHYSICAL PROPERTIES WITH THE HYDROXYL GROUPS AND HYGROEXPANSIVITY OF SHEETS PREPARED FROM THE HYDROXYL CONTENT 40-MINUTE HEATING INTERVAL

Curve 1  Bursting Strength
Curve 2  Hygroscopicity
Curve 3  Hygroexpansivity

Percentage of Hydroxyl Groups Replaced by Acyl Groups
(Percentage of acyl by weight in brackets)
development of external surface during beating, may have become more pronounced and thus may have increased the hydrophilic properties of the beaten as compared with the unbeaten material. At an acetyl content of 1.6 per cent, the maximum increase in hygroscopicity of the unbeaten acetylated fibers over the unbeaten raw material (at 90 per cent relative humidity) was from 1.6 to 20.5 per cent, or an increase of about 10 per cent. This increase was maintained up to an acetyl content of approximately 8 per cent.

After the maximum is reached, the moisture content falls off rather rapidly until, at about 10 per cent acetyl content, the moisture content is practically that of the original material. Thereafter, the values continue to fall and reach a minimum at the highest acetyl content (25.65 per cent). The minimum moisture content for the unbeaten stock is 19.6 per cent (at 90 per cent relative humidity and 25.65 per cent acetyl); this corresponds to a decrease of about 40 per cent, as compared with the unacetylated material. In the case of the beaten stock, at the same acetyl content and humidity, the minimum moisture content is 12 per cent; this corresponds to a decrease of about 34 per cent from the value for the beaten unacetylated material.

The expected

To demonstrate the existence of a relation between the hygroscopicity and the physical strength properties at various acetyl contents, as mentioned above, the bursting strength was selected as the most characteristic of the physical strength properties of the sheets. The bursting strength values were plotted against the percentage of hydroxyl groups of the cellulose replaced by acetyl groups. This
relationship is seen in Figure 6 (for the unbeaten stock) and in Figure 7 (for the beaten stock). The range in which the maximum in bursting strength occurs coincides with the range in which the maximum in hygroscopicity was observed; with further increasing acetyl content, both physical strength properties and hygroscopicities drop in about the same manner. These results furnish support for the hypothesis which explains the development of the maximum physical strength properties of increased accessibility of hydroxyl groups. Again, to realize this effect, it is not necessary to beat the stock. This fact is in good agreement with the observation that the maximum physical strength may be developed before disintegration.

THE HYDROEXPANSIVITY OF THE ACETYLIZED PULPS AND ITS RELATION TO OTHER PROPERTIES

If the introduction of small amounts of acetyl into the fibers increases the accessibility of the hydroxyl groups, as postulated earlier, one would expect to find an increase in the hygroexpansivity of sheets prepared from such fibers as the acetyl content is increased up to a certain point, but a decrease as more acetyl is introduced. A relationship should then exist between all three properties of the sheets of acetylated fibers—i.e., the hygroexpansivity, the hygroscopicity, and the physical strength properties.

To prove the existence of this relationship, the hygroexpansivity of the hand-sheets prepared from the acetylated materials were determined. The results are summarized in Table VII and shown in graphically curves 3 of Figure 6 and 7. The relation between the
Hygroexpansivity, hygroscopicity, and bursting strength is also shown in these two figures.

In the case of the unbeaten stocks (Figure 6), this relationship is very close. The hygroexpansivity first increased and reached a maximum at an acetyl content between 2 and 6 per cent, which is close to the point where the maximum hygroscopicity and maximum bursting strength are observed. It then falls and follows closely the drop in hygroscopicity and bursting strength as the acetyl content approaches the highest value (25.65 per cent). The maximum decrease in hygroexpansivity from that of the unacetylated material was from 0.465 to 0.30 per cent, corresponding to a decrease of about 35 per cent.

The relation between the hygroexpansivity and the other properties is less close for the beaten materials (Figure 7). The hygroexpansivity starts with a higher value than shown by the unbeaten materials and decreases to a minimum value. The original value (of the raw material) was 0.52 per cent, and the values at the maximum hygroscopicity were between 0.4 and 0.45 per cent. Above an acetyl content of 13 to 20 per cent, the hygroexpansivity dropped sharply. At the highest acetyl content (25.65 per cent), the value was 0.255 per cent. The maximum decrease in hygroexpansivity was from 0.52 to 0.255 per cent, or a decrease of approximately 50 per cent. This is somewhat more than that observed with the unbeaten materials.

The relation between hygroexpansivity, hygroscopicity, and bursting strength was not so close with the beaten as with the unbeaten
### Table VII

**Results of Hygroexpansivity Measurements of Sheet Prepared from Acetylated Pulps**

**Adsorption Data**

**Effect of Humidity Change on the Percentage Change in Length of Handheets**

<table>
<thead>
<tr>
<th>Acetyl Content of Pulp, ( % )</th>
<th>Humidity Change 10% to 30%</th>
<th>0 Min.</th>
<th>Humidity Change 10% to 60%</th>
<th>0 Min.</th>
<th>Humidity Change 10% to 30%</th>
<th>40 Min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unacetylated pulp</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.52</td>
<td>0.13</td>
<td>0.125</td>
<td>0.305</td>
<td>0.35</td>
<td>0.455</td>
<td>0.46</td>
</tr>
<tr>
<td>4.65</td>
<td>0.145</td>
<td>0.325</td>
<td>0.315</td>
<td>0.46</td>
<td>0.445</td>
<td>0.44</td>
</tr>
<tr>
<td>5.27</td>
<td>0.13</td>
<td>0.325</td>
<td>0.305</td>
<td>0.44</td>
<td>0.445</td>
<td>0.44</td>
</tr>
<tr>
<td>6.9</td>
<td>0.115</td>
<td>0.32</td>
<td>0.285</td>
<td>0.38</td>
<td>0.445</td>
<td>0.44</td>
</tr>
<tr>
<td>7.05</td>
<td>0.12</td>
<td>0.305</td>
<td>0.295</td>
<td>0.44</td>
<td>0.445</td>
<td>0.44</td>
</tr>
<tr>
<td>10.6</td>
<td>0.13</td>
<td>0.315</td>
<td>0.31</td>
<td>0.46</td>
<td>0.445</td>
<td>0.44</td>
</tr>
<tr>
<td>12.57</td>
<td>0.09</td>
<td>0.285</td>
<td>0.31</td>
<td>0.43</td>
<td>0.445</td>
<td>0.44</td>
</tr>
<tr>
<td>14.5</td>
<td>0.07</td>
<td>0.26</td>
<td>0.295</td>
<td>0.37</td>
<td>0.435</td>
<td>0.44</td>
</tr>
<tr>
<td>15.37</td>
<td>0.06</td>
<td>0.21</td>
<td>0.295</td>
<td>0.44</td>
<td>0.445</td>
<td>0.44</td>
</tr>
<tr>
<td>20.1</td>
<td>0.06</td>
<td>0.27</td>
<td>0.31</td>
<td>0.34</td>
<td>0.455</td>
<td>0.45</td>
</tr>
<tr>
<td>20.56</td>
<td>0.04</td>
<td>0.175</td>
<td>0.30</td>
<td>0.29</td>
<td>0.455</td>
<td>0.30</td>
</tr>
</tbody>
</table>

*Zero interval or unbeaten pulp

**40-minute beating interval**
materials. It was thought that the apparent density, which (as shown in Table IV) is different for the various materials, might furnish an explanation. It would appear that, in a sheet of low density, there is more room for the individual fibers to expand or contract without causing a change in the over-all dimensions. A comparison of the apparent densities of the hashed sheets prepared from the beaten materials with those of the unbeaten materials does not seem to offer the same explanation. However, observed behavior of the fibers as expected—due to the deviation in the relation between the hygroexpansivity—thus, it must be assumed that factors other than the apparent density have a more pronounced influence. These factors are probably the result of the beating procedure and the formation of a sheet from the beaten fibers. Further investigation would be required to determine these factors and their influence.

The data seem to indicate that, although the apparent density undoubtedly influences the measurements to some extent, the decrease in hygroexpansivity is chiefly a result of the reduced swelling of the highly acetylated fibers.

In the light of a possible commercial utilization of the reduced hygroexpansivity of a sheet of paper prepared from acetylated fibers, it is unfortunate that, as the hygroexpansivity is reduced, the physical strength properties also decrease. In other words, a reduction of the hygroexpansivity by approximately 50 per cent, which would be very appreciable for commercial purposes, is realized only when the physical strength properties are also at a minimum. This large reduction in hygroexpansivity occurs when 40 to 50 per cent of the hydroxyl groups are replaced by acetyl groups.
As was shown by Eletzinger and later confirmed by Aiken, the acetylated pulps are wetted and swell in acetone; when beaten in this medium, they produce sheets which exhibit good strength properties. Similar experiments were also carried out in the present study. It was expected that a reduction in hygroexpansivity would be produced similar to that occurring with the water-beaten acetylated materials, but without the disadvantage of the serious lack of physical strength.

The following experiments were carried out with the object of possibly increasing the strength properties of the sheets and, in some cases, of reducing the amount of acetone or eliminating the necessity of employing acetone as a processing medium, having in view a possible commercial utilization. In addition to the use of acetone as the processing medium, it was thought that it might suffice to employ a mixture of acetone and water, or to beat the acetylated material in acetone but prepare the sheet from a water suspension of the acetone-beaten stock. Another modification consisted of processing the acetylated fibers in water and subsequently dipping the resulting sheet in acetone and pressing it. Included in this series of experiments were the dipping of water-processed sheets in chloroform and the use of a wetting agent in combination with the beating and sheet preparation in water alone.

Two acetylated materials, one having 20.1 and the other 25.65
per cent acetyl content, were employed. They were processed in the usual way (unless otherwise stated), with the exception that the effluents from the sheet machine were not discarded but were reused. Sheets were prepared from the pulp at the 45-minute beating intervals and tested for physical strength properties according to the customary procedure. The results are presented in Table VIII and Table VIIIA; the latter shows the data calculated on the cellulose basis.

Acetone Medium

The pulp containing 20.1 per cent acetyl, when processed in acetone, showed a definite increase in strength properties over those obtained when it was processed in water. For instance, the bursting strength of the acetone-processed sheets from the unbeaten and beaten intervals were 14.3 and 50.8, respectively, as compared with 9.5 and 25.0 for the water-processed sheets at the corresponding intervals.

For the material containing 25.65 per cent acetyl, the strength properties of the sheets beaten and processed in acetone were considerably above those of the same material prepared in water. For example, the bursting strengths of the acetone-processed sheets from the unbeaten and the beaten (45-minute) materials were 13.9 and 55.7, respectively, as compared with 4.6 and 5.2 for the water-processed sheets. This confirms Aiken's findings.

The beating experiment with the material containing 20.1 per cent acetyl, using a 10 per cent acetone-water medium, gave sheets which had strength properties somewhat better than those obtained when water alone was employed as the processing medium. As an example, the
TABLE XVI
COMPARISON OF STRENGTH PROPERTIES OF SHEETS PROCESSED IN WATER AND IN CHLOROFORM

<table>
<thead>
<tr>
<th></th>
<th>Basis Weight</th>
<th>Apparent Density</th>
<th>Burst Factor</th>
<th>Tear Factor</th>
<th>Tensile Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Acetate</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Processed in water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zero interval</td>
<td>43.4</td>
<td>10.1</td>
<td>9.7</td>
<td>2.68</td>
<td>11.2</td>
</tr>
<tr>
<td>40-minute interval</td>
<td>43.5</td>
<td>15.3</td>
<td>16.9</td>
<td>0.89</td>
<td>51.1</td>
</tr>
<tr>
<td>Acetone</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Processed in Acetone</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zero interval</td>
<td>42.2</td>
<td>7.67</td>
<td>9.5</td>
<td>0.834</td>
<td>5.96</td>
</tr>
<tr>
<td>40-minute interval</td>
<td>42.2</td>
<td>12.85</td>
<td>27.6</td>
<td>0.659</td>
<td>14.4</td>
</tr>
<tr>
<td>Processed in 1/3 Acetone-Water</td>
<td></td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>40-minute interval</td>
<td>46.1</td>
<td>13.5</td>
<td>31.0</td>
<td>0.67</td>
<td>16.7</td>
</tr>
<tr>
<td>Acetone</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Processed in Acetone</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zero interval</td>
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<td>6.51</td>
<td>4.6</td>
<td>0.38</td>
<td>1.76</td>
</tr>
<tr>
<td>40-minute interval</td>
<td>42.0</td>
<td>3.77</td>
<td>5.2</td>
<td>0.22</td>
<td>2.3</td>
</tr>
<tr>
<td>Processed in water plus 0.01% Baking Agent</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40-minute interval</td>
<td>41.3</td>
<td>9.16</td>
<td>6.5</td>
<td>0.345</td>
<td>3.0</td>
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<tr>
<td>Acetate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Processed by Soaking 40 minutes in Acetone, Removing the Acetone, and Taking up Sheet in Water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40-minute interval</td>
<td>42.8</td>
<td>11.38</td>
<td>18.1</td>
<td>1.26</td>
<td>15.63</td>
</tr>
<tr>
<td>Acetone</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Processed in Water—Air-dry Sheets Dipped in Chloroform</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zero interval</td>
<td>42.2</td>
<td>6.51</td>
<td>16.0</td>
<td>1.34</td>
<td>3.4</td>
</tr>
<tr>
<td>40-minute interval</td>
<td>39.4</td>
<td>10.65</td>
<td>17.0</td>
<td>0.45</td>
<td>3.6</td>
</tr>
<tr>
<td>Processed in Water—Air-dry Sheets Dipped in Acetone</td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zero interval</td>
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<td>7.3</td>
<td>10.9</td>
<td>0.75</td>
<td>5.36</td>
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<td>40-minute interval</td>
<td>41.1</td>
<td>10.3</td>
<td>10.7</td>
<td>0.75</td>
<td>5.35</td>
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</tbody>
</table>
TABLE VIII

COMPARISON OF STRENGTH PROPERTIES OF SHEETS PROCESSED IN WATER AND IN ORGANIC LIQUIDS

(Original Cellulose Basis)

<table>
<thead>
<tr>
<th></th>
<th>Basis Weight</th>
<th>Apparent Density</th>
<th>Burst Factor</th>
<th>Tear Factor</th>
<th>Tensile Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Unacetylated Bleached Mitscherlich pulp - Processed in Water</strong></td>
<td></td>
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<tr>
<td>Zero interval</td>
<td>43.4</td>
<td>1.11</td>
<td>26.2</td>
<td>2.68</td>
<td>11.2</td>
</tr>
<tr>
<td>40-minute interval</td>
<td>43.5</td>
<td>16.3</td>
<td>161.0</td>
<td>0.39</td>
<td>51.1</td>
</tr>
<tr>
<td><strong>20.1% Acetyl Content - Processed in Water</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zero interval</td>
<td>34</td>
<td>6.2</td>
<td>11.8</td>
<td>1.0</td>
<td>4.92</td>
</tr>
<tr>
<td>40-minute interval</td>
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<td>10.4</td>
<td>11.0</td>
<td>0.318</td>
<td>17.9</td>
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<tr>
<td><strong>20.1% Acetyl Content - Processed in Acetone</strong></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zero interval</td>
<td>34.1</td>
<td>7.2</td>
<td>19.1</td>
<td>0.67</td>
<td>8.4</td>
</tr>
<tr>
<td>40-minute interval</td>
<td>35.0</td>
<td>11.23</td>
<td>75.5</td>
<td>1.2</td>
<td>25.7</td>
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<td><strong>20.1% Acetyl Content - Processed in 10% Acetone-Water</strong></td>
<td></td>
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<tr>
<td>40-minute interval</td>
<td>37.1</td>
<td>14.9</td>
<td>18.5</td>
<td>1.03</td>
<td>20.7</td>
</tr>
<tr>
<td><strong>25.65% Acetyl Content - Processed in Water</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zero interval</td>
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<td>4.87</td>
<td>6.1</td>
<td>0.51</td>
<td>2.35</td>
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<td>7.52</td>
<td>6.9</td>
<td>0.324</td>
<td>3.1</td>
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<td><strong>25.65% Acetyl Content - Processed in Acetone</strong></td>
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<td>6.2</td>
<td>17.2</td>
<td>1.53</td>
<td>9.3</td>
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<td>16.4</td>
<td>74.4</td>
<td>1.03</td>
<td>31.9</td>
</tr>
<tr>
<td>60-minute interval</td>
<td>32.9</td>
<td>9.66</td>
<td>68.2</td>
<td>1.22</td>
<td>23.5</td>
</tr>
<tr>
<td><strong>25.65% Acetyl Content - Processed in Water plus 0.015% Setting Agent</strong></td>
<td></td>
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</tr>
<tr>
<td>40-minute interval</td>
<td>31.3</td>
<td>6.86</td>
<td>2.7</td>
<td>0.46</td>
<td>4.0</td>
</tr>
<tr>
<td><strong>25.65% Acetyl Content - Processed by Beating 40 minutes in Acetone - Removing the Acetone and Making up the Sheets in Water</strong></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40-minute interval</td>
<td>31.6</td>
<td>8.5</td>
<td>14.2</td>
<td>1.68</td>
<td>20.9</td>
</tr>
<tr>
<td><strong>25.65% Acetyl Content - Processed in Water - Air-dry Sheets Dipped in Chloroform</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zero interval</td>
<td>32.1</td>
<td>6.6</td>
<td>33.4</td>
<td>3.46</td>
<td>11.2</td>
</tr>
<tr>
<td>40-minute interval</td>
<td>33.5</td>
<td>8.0</td>
<td>22.7</td>
<td>0.50</td>
<td>11.5</td>
</tr>
<tr>
<td><strong>25.65% Acetyl Content - Processed in Water - Air-dry Sheets Dipped in Acetone</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zero interval</td>
<td>31.5</td>
<td>5.3</td>
<td>14.6</td>
<td>1.0</td>
<td>4.51</td>
</tr>
<tr>
<td>40-minute interval</td>
<td>30.8</td>
<td>7.7</td>
<td>14.3</td>
<td>0.47</td>
<td>7.14</td>
</tr>
</tbody>
</table>
The bursting strength of the beaten stock was 31.0 for the 10 per cent acetone-water-processed sheets and 25.0 for the water-processed sheets.

Wetting Agent

When water containing 0.01 per cent wetting agent was used for the processing of the material having an acetyl content of 25.65 per cent, a bursting strength of 6.5 was found for the sheets from the beaten stock. The other strength properties were correspondingly low.

Beating in Acetone—Sheetmaking in Water

An acetylated material (25.65 per cent acetyl content) was beaten in acetone, the acetone was removed, and the sheets made up in water. The sheets had a bursting strength of 33.1 and a tensile strength of 15.63, as compared with 55.7 and 23.9 for the respective tests when the pulp was processed in acetone only.

Dipping Water-Processed Sheets in Acetone and Chloroform

When the sheets were made up in water and dipped in acetone, they showed a little more than twice the strength of the same product when processed in water alone. However, the sheets were still rather weak, having bursting strengths of only 19.9 and 10.7 and tensile strengths of 3.33 and 5.35 at the zero and 20-minute intervals, respectively.

The procedure used may be summarized as follows:
The air-dry, water-processed sheets were placed on the metal drying plates used in the British sheetmaking equipment, and a very fine mesh screen was placed over the sheet. The organic liquid was then poured over the screen and allowed to penetrate into the sheet. The screen helped prevent the liquid from spoiling the sheet formation. The screen was removed, and the wet sheets were placed in a press between solvent-soaked blotters and pressed at a pressure of 50 lb./sq. in. for 5 minutes. The blotters were then changed, and the sheets were pressed again at 50 lb./sq. in. for 2 minutes. After the second pressing, the sheets were placed in drying rings and allowed to air dry, after which they were conditioned at 75° C. and 50 per cent relative humidity before testing.

The chloroform-treated sheets (following the procedure described above) gave a much greater increase in strength than the acetone-treated sheets. In fact, the unbeaten stock showed a bursting strength of 25.0 and a tensile strength of 8.3, as compared with a bursting strength of 12.9 and a tensile strength of 6.95 for the same stock beaten in acetone. The water-processed sheets from the beaten material showed a good increase in strength properties when treated with chloroform. The bursting strength increased from 5.2 to 17.0 and the tensile strength from 2.3 to 5.6. However, it can be seen that the increase in bursting strength of the water-beaten material (by treating the water-processed sheets with chloroform) was not as great as the increase observed in the case of the unbeaten sheets. The lack of strength development upon processing the beaten material in water may be partially explained by the fact that the acetylated fibers, when process-
ed in water, are not fibrillated but are rather badly broken (see Figures 3, 4, and 5).

Further microscopic observations were made on the acetylated fibers which had been processed in acetone. Thus, the effect of beating in acetone and in water could be compared. As pointed out earlier, the unacetylated material appeared well fibrillated when beaten in water for 40 minutes in the Lampen mill (Figure 4). The photomicrograph (Figure 5) shows the fibers (25.65 per cent acetyl content) which had been beaten in acetone for 40 minutes. These fibers appear to be fibrillated and brushed out very much like those of the water-beaten unacetylated material, although to a somewhat smaller degree.

The results of the experiments described above seem to show that the best strength properties are obtained if the acetylated material is processed in acetone as described by Bletzinger and that the modifications tried give less favorable results.

COMPARISON OF THE HYDROEXPANSIVITY OF ACETILATED FIBER SHEETS PROCESSED IN WATER AND IN ACETONE

The results of the hydroexpansivity measurements made on the materials which had been processed in acetone are shown in Table IX. This table also contains the results of previous measurements on the same products processed in water. In addition, the bursting strength values taken from Table VIII are given.

The unbeaten materials processed in acetone showed a somewhat lower hydroexpansivity than the corresponding products processed
Figure 8

Acetylated Pulp - Processed in Acetone
25.65 % Acetyl Content
(40 Minute Interval)
TABLE IX
EFFECT OF ACETONE ON HYDROEXPANSIVITY

Adsoption Data

Effect of Humidity Changes on the Percentage Change in Length of Handsheets

<table>
<thead>
<tr>
<th>Humidity Change</th>
<th>Humidity Change</th>
<th>Humidity Change</th>
<th>Humidity Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>10% to 0%</td>
<td>0% to 10%</td>
<td>0% to 60%</td>
<td>10% to 60%</td>
</tr>
<tr>
<td>Bursting</td>
<td>0.10 Min.</td>
<td>0.40 Min.</td>
<td>0.40 Min.</td>
</tr>
<tr>
<td>Water</td>
<td>9.5</td>
<td>25.0</td>
<td>0.06</td>
</tr>
<tr>
<td>Acetone</td>
<td>15.4</td>
<td>60.3</td>
<td>0.039</td>
</tr>
</tbody>
</table>

20.1% Acetyl Content

| Water           | 4.6             | 3.2             | 0.04            |
| Acetone         | 12.9            | 55.7            | 0.035           |

25.65% Acetyl Content

| Water           | 4.6             | 3.2             | 0.04            |
| Acetone         | 12.9            | 55.7            | 0.035           |

* Zero interval or unbeaten
** 40-minute beating interval

The results obtained with the material containing 20.1% Acetyl were compared with the results obtained with the material containing 25.65% Acetyl. In water, but the values of the materials which had been beaten agreed fairly well. The results obtained with the material containing 25.65% Acetyl are better than those for the material with lower acetyl content. The best reductions in hydroexpansivity were from 0.145 to 0.22 per cent; and from 0.22 per cent to 0.44 per cent for the unbeaten sheets, and 0.27 per cent to 0.40 per cent for the beaten sheets.

An inspection of the bursting strength values in Table IX shows that such reductions in hydroexpansivity could be realized while the sheets still possess fairly good strength properties.
THE EFFECT OF ESTERIFICATION WITH HIGHER FATTY ACIDS UPON THE PROPERTIES OF SHEETS PREPARED FROM SUCH ESTERIFIED FIBERS

As has been explained in the introduction, it was hoped that, by the introduction of acyl radicals of increasing size, an increasing lower degree of substitution would suffice to bring about the same effect of esterification upon the physical strength properties, the hygroscopicity, and the hygroexpansivity of the sheets as was observed with the acetylated materials. This is based particularly upon the work of Sheppard and Newsome (3, 4). They showed that the percentage moisture regain at 50 per cent relative humidity dropped from about 10 per cent for the tricellate to between 3 and 4 per cent for the tributyrate and to about 1 per cent for the tristearate. In view of the relation which has been shown to exist between the hygroscopicity of sheets prepared from acetylated fibers and their hygroexpansivity, it was expected that such a relation would also be found with sheets prepared from other partially esterified fibers. Moreover, it was hoped to show the relationship between these two characteristics and the physical strength properties in both the lower and the higher range of substitution. It was thought advisable to investigate the effect of the esterification with a very high fatty acid first and to compare the results with those of esterification—i.e., to compare two extreme cases. The stearoyl radical was chosen for this purpose.

THE PREPARATION OF CELLULOSE STERONATES OF VARYING STERONYL CONTENT

As in the case of the acetates, the most important
prerequisite in this study was that the stearoyl group be introduced into the cellulose material without destroying its original fibrous structure and unduly decreasing its physical strength properties. Of the several methods considered (2, 27, 28), that using stearic anhydride (25) was discarded because of the slow rate of reaction and the high temperature required. The method finally selected was a modification of the procedure suggested by Ornin and Ritter (27) for the preparation of higher fatty acid esters; the derivative is formed by the action of the acid chloride on cellulose in the presence of pyridine and a diluent (benzene), at the refluxing temperature of the mixture. No exact data are available to show the extent of the cellulose degradation under these conditions. It is very probable, however, that it suffered a substantial decrease in degree of polymerization.

In view of the fact that, in the present study, a fibrous product was desired which was degraded as little as possible and which had a comparatively low degree of substitution, the esterifications were carried out at a lower temperature.

The procedure used in the preparation of the stearates was as follows. A quantity of Mitscherlich milp (equivalent to 100 grams of oven-dry material) was placed in a 0.1-gallon jar, covered with pyridine, and allowed to soak overnight to remove the moisture from the milp and to swell the fibers. The milp was delivered by subjecting the mixture to the action of a Lightning mixer for 10 minutes. The pyridine was then removed from the milp as completely as possible on a Schinner funnel. Between 250 and 300 ml of pyridine remained in the milp. The milp was weighed, placed in a 1-gallon jar, and treated
with a mixture of pyridine, benzene, and stearoyl chloride. (Upon
the addition of the pyridine to a mixture of commercial stearoyl chlo-
ride and benzene, a precipitate of stearoylpyridinium chloride was
formed, accompanied by a rise in temperature of the mixture. The
esterifying mixture was cooled to room temperature before adding to the
pulp pad.) The mixture was stirred with a Lightnin mixer for 5
minutes and the temperature measured. The temperature of this sus-
pension depends upon the amount of diluent used and upon the amount of
free pyridine retained by the pulp. The rise in temperature of the
pulp suspension which accompanied the addition of the stearoylation
mixture was never greater than 15° C., and the maximum temperature of
the reactions was about 40° C.

At the end of the esterification period, the stearoylation
mixture was removed by filtering the suspension on a Buchner funnel.
The stearoylated pulp pad was transferred to a 3-liter beaker and
washed once with hot benzene and once with hot (recovered) alcohol-
benzene to remove the esterifying mixture as far as possible. The
juice was then concentrated with benzene for
sulfur was then placed in a Soxhlet and extracted for 24 hours, with
benzene. After the 24-hour benzene-extraction, the excess benzene was
filtered off and the pulp pad washed with alcohol. The pulp was re-
turned to the Soxhlet and extracted for another 24 hours with ethanol.
After the 24-hour alcohol-extraction, the excess alcohol was filtered
off and the pulp washed with ether. The material was again returned
to the Soxhlet and extracted for an additional 24 hours with ether.
After the ether extraction, the excess ether was removed by suction on
a Buchner funnel and the esterified pulp allowed to dry in the air for
several hours.
The stearates were analyzed according to the standard isolation procedure. As pointed out previously, because of the insolvibility of the fibrous esters and the cellulose regenerated therefrom in the ordinary cellulose and ester solvents, the degree of polymerization of the esterified materials could not be determined. However, this lack of solubility in itself and the fibrous condition of the ester indicated that the degree of polymerization was high. The stearates of a higher degree of substitution had a fatty feel.

A summary of the esterifying conditions, as well as the stearoyl contents and the percentage of hydroxyl groups covered in the stearoylated fibers, is given in Table X. Originally, it was planned to control the stearoyl content of the products by changing the mole ratio of stearoyl chloride to cellulose and the time of esterification, and by maintaining a constant temperature. However, when the series were made up, it was discovered that the amount of pyridine remaining in the pulp and after the presoaking period, the amount of diluent, and the rate at which the esterification mixture was added were very important, and slight changes in these factors caused quite large variations in temperature. These changes in temperature influenced the rate of stearoylation considerably. Fortunately, the pulp stearoylated by the above method happened to have stearoyl contents in a suitable range for the present study.

The lowest degree of substitution corresponded to only a small fraction of one stearoyl group per anhydroglucose unit. But it is significant that the percentage weight increase—because of the size
<table>
<thead>
<tr>
<th>Apparent Stearoyl Content</th>
<th>Hydroxy Group Covered</th>
<th>Mole Ratio of Cellulose to Stearoyl Chloride</th>
<th>Stearoyl Chloride, c.c. Mr/g. of Cellulose</th>
<th>Benzene, ml/g. of Cellulose</th>
<th>Pyridine, ml/g. of Cellulose</th>
<th>Time, hr.</th>
<th>Temperature, °C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.8</td>
<td>1.1</td>
<td>1:2</td>
<td>4</td>
<td>39.3</td>
<td>6.6</td>
<td>24</td>
<td>24</td>
</tr>
<tr>
<td>37.8</td>
<td>10</td>
<td>1:2</td>
<td>4</td>
<td>39.3</td>
<td>6.6</td>
<td>2</td>
<td>36+3</td>
</tr>
<tr>
<td>4.6</td>
<td>15</td>
<td>1:2</td>
<td>4</td>
<td>25.0</td>
<td>6.6</td>
<td>1</td>
<td>36+3</td>
</tr>
<tr>
<td>51.5</td>
<td>31.7</td>
<td>1:2</td>
<td>4</td>
<td>25.0</td>
<td>6.6</td>
<td>4</td>
<td>36+3</td>
</tr>
<tr>
<td>52.7</td>
<td>32.8</td>
<td>1:2</td>
<td>4</td>
<td>39.3</td>
<td>6.6</td>
<td>67</td>
<td>24</td>
</tr>
<tr>
<td>60.2</td>
<td>32.7</td>
<td>1:3.h</td>
<td>7</td>
<td>19</td>
<td>11.5</td>
<td>24</td>
<td>40°-24°*</td>
</tr>
</tbody>
</table>

*The temperature of the reaction mixture rose to 40° C. when the esterifying agents were added to the cellulose, and was then allowed to cool down to room temperature. As a result of this, the n-butyl pyridine solvent was replaced with n-butanol.
of the stearoyl radical—is rather high. The highest degree of substitution corresponded to about one stearoyl group to one anhydro-glucos unit. The monostearate requires 62.3 per cent stearoyl (or 66.3 per cent combined stearic acid).

PHYSICAL STRENGTH PROPERTIES OF SHEETS OF FIBROUS STEARATES PROCESSED IN WATER

To study the effect of stearoylation upon the physical properties of pulp, the stearates previously described (with the exception of Preparation 5) were processed in water using the standard procedure at the zero and 40-minute intervals. Handsheets were prepared from these stocks and their physical properties determined. The results of the strength evaluations of these pulps are given in Table XI and XIA. The values in Table XIA are calculated on the original cellulose basis. The bursting strength values, in their relation to the percentage of hydroxyl groups covered by stearoyl groups, are shown in Figures 9 and 10.

The data in Tables XI and XIA and in Figures 9 and 10 show that the hydrating and bonding characteristics of the fibers have been largely destroyed by the introduction of the stearoyl group. With only 4.1 per cent of the hydroxyl groups replaced, the stearoylated fibers were very hydrophobic, and the hydrophobic character appeared to increase still further with increasing stearoyl content. The fibers which had been only slightly stearoylated floated on the water and were very difficult to wet. They were not completely wet even after they had been submerged for at least 12 hours prior to beating. The sheets
<table>
<thead>
<tr>
<th>Apparent Stearoyl Content, %</th>
<th>Hydroxyl Groups Covered, %</th>
<th>Basis Apparent Burst Tear Tensile Caliper Weight Density Factor Factor Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original pulp</td>
<td>-</td>
<td>4.2</td>
</tr>
<tr>
<td>15.2</td>
<td>4.1</td>
<td>7.7</td>
</tr>
<tr>
<td>17.3</td>
<td>10</td>
<td>9.4</td>
</tr>
<tr>
<td>42.6</td>
<td>15</td>
<td>13.25</td>
</tr>
<tr>
<td>51.5</td>
<td>21.7</td>
<td>16.4</td>
</tr>
<tr>
<td>60.2</td>
<td>30.7</td>
<td>22.9</td>
</tr>
</tbody>
</table>

Beaten for 40 minutes in the Lampen-Mill

| Original pulp              |                             | 2.66                            |
| 15.2                       | 4.1                        | 5.2                             |
| 32.3                       | 10.0                       | 5.2                             |
| 42.6                       | 15.0                       | 9.7                             |

For reference:

12.0 lb. 8.0 in. 2.0 mm
TABLE XIA

PHYSICAL STRENGTH PROPERTIES OF STARCHYLATED FIBRES
IN THE UNBEATEN AND THE BEATEN STATE

(Calculated on Original Cellulose Basis)

Unbeaten Stock

<table>
<thead>
<tr>
<th>Apparent Starchyl Group Content</th>
<th>Hydroxyl Covered %</th>
<th>Caliper</th>
<th>Basis Weight</th>
<th>Apparent Density</th>
<th>Burst Factor</th>
<th>Tear Factor</th>
<th>Tensile Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.8</td>
<td>4.1</td>
<td>7.7</td>
<td>42.6</td>
<td>5.6</td>
<td>7.0</td>
<td>0.55</td>
<td>2.58</td>
</tr>
<tr>
<td>32.8</td>
<td>10</td>
<td>9.4</td>
<td>31.8</td>
<td>3.4</td>
<td>5.0</td>
<td>0.31</td>
<td>1.26</td>
</tr>
<tr>
<td>42.6</td>
<td>15</td>
<td>13.25</td>
<td>42.7</td>
<td>3.2</td>
<td>3.5</td>
<td>0.16</td>
<td>0.94</td>
</tr>
<tr>
<td>51.5</td>
<td>21.7</td>
<td>16.4</td>
<td>43.5</td>
<td>2.6</td>
<td>4.1</td>
<td>0.41</td>
<td>1.6</td>
</tr>
<tr>
<td>60.2</td>
<td>30.7</td>
<td>22.0</td>
<td>44.0</td>
<td>2.0</td>
<td>-</td>
<td>0.22</td>
<td>0.57</td>
</tr>
</tbody>
</table>

Beaten for 40 Minutes in the Leonard Mill

<table>
<thead>
<tr>
<th>Apparent Starchyl Group Content</th>
<th>Hydroxyl Covered %</th>
<th>Caliper</th>
<th>Basis Weight</th>
<th>Apparent Density</th>
<th>Burst Factor</th>
<th>Tear Factor</th>
<th>Tensile Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.8</td>
<td>4.1</td>
<td>5.2</td>
<td>42.3</td>
<td>3.2</td>
<td>10.5</td>
<td>0.30</td>
<td>5.5</td>
</tr>
<tr>
<td>32.8</td>
<td>10.0</td>
<td>5.2</td>
<td>29.8</td>
<td>5.7</td>
<td>10.4</td>
<td>0.12</td>
<td>4.75</td>
</tr>
<tr>
<td>42.5</td>
<td>15.0</td>
<td>9.7</td>
<td>46</td>
<td>4.72</td>
<td>2.3</td>
<td>0.14</td>
<td>1.7</td>
</tr>
</tbody>
</table>
Percentage of Hydroxyl Groups Replaced by Acyl Groups
(Percentage and by weight in brackets)
Comparison of the Initial Properties with the Hygroscopicity of the Hydrated Silica
and Density of Sheets Prepared from Silicified Wood

40-Minute Testing Interval

Curve 1: Bursting Strength
Curve 2: Hygroscopicity
Curve 3: Hygroscopicity

Percentage Change in Length (Humidity Change - 10% to 90%)

Percentage of Hydroxyl Groups Replaced by Acetyl Groups
(Percentage and by weight in crystals)
prepared from the unbeaten stocks were quite bulky and had a low apparent density. The stocks showed practically no strength development on beating, even though the apparent density of the sheets was increased slightly.

Microscopic observations of the beaten fibers showed that even the stearate with 15.8 per cent stearoyl content (only 4.1 per cent of the hydroxyl groups replaced) had been crushed and broken during the beating operation in much the same manner as the more highly acetylated fibers were damaged when they were processed in water.

The results seem to show that, even if only a relatively small number of its hydroxyl groups are replaced by long chain acid molecules, the hydrophilic properties of cellulose are so reduced that the bonding forces between the hydroxyl groups are virtually eliminated. Indeed, it was impossible to process the stearoylated fibers in water even to an extent that a sheet with modest strength properties could be obtained. This result would appear to demonstrate the predominating influence exerted by such highly hydrophobic acid radicals as the stearoyl. It would seem that even relatively small amounts of stearoyl cause the cellulose fibers to lose their characteristic properties and to acquire those of the stearic acid.

The bursting strength curves in Figures 9 and 10 do not show the phenomenon of first reaching a maximum before dropping to lower values, as was observed with the acetylated fibers; this is probably because of the fact that the stearoyl content was not low enough. In view of the pronounced hydrophobic effect exerted by the
stearoyl radical, it would probably be difficult to limit the degree of substitution to that low range within which a maximum could be expected to appear.

The above interpretation of the physical strength data is made on the assumption that the cellulose had not been substantially degraded during the process of stearoylation. It is unfortunate that the degree of polymerization could not be determined. Although the evidence on which the above interpretation is based is only of an indirect nature, it appears to be quite convincing.

TREATMENT OF STEARATES WITH ORGANIC SWELLING AGENTS

It has been shown that the stearates, when processed in water, did not develop strength on beating. The possibility of using an organic swelling agent for solvating the esterified material and of obtaining results similar to those produced by beating the acetylated fibers in acetone thus appeared feasible.

For roughly evaluating the effect of a great number of organic liquids within a relatively short time, a simplified technique was employed. It is well known that, when the water is removed from a thoroughly stirred pulp suspension on a Büchner funnel and the pad thus formed is dried, the latter has a certain amount of strength. The same effect was shown by the acetylated fibers when treated with acetone or chloroform. In contrast, when acetylated fibers were suspended in water, the pad resulting from the removal of the water is fluffy and has no strength. This technique of suspending fibers in...
liquids and of making pulp beds was applied to the stearoylated fibers, using various organic swelling agents.

The material containing 60.2 per cent stearoyl was treated with the following organic liquids: cyclohexene, monochlorobenzene,* methyl amyl ketone, diacetone alcohol, butyl cellosolve, cyclohexanone, glycol diformate, di-2-chloroethyl formal, diethyl cellosolve, methyl cellosolve formal, triglycol dichloride,* methyl carbitol acetate,* diglycol diacetate, trichloroethane,* dichloroisopropyl ether,* xylene,* benzenes,* carbon tetrachloride,* chloroform,* and acetone.* All the organic liquids, except glycol diformate, wetted the stearate and made possible the dispersion of the fibers. Those liquids followed by an asterisk caused the greatest swelling. However, when the organic liquids were removed from the fibers, the resulting pulp beds were loose and fluffy and had very poor strength, regardless of the extent to which the fibers were swollen while in contact with the organic liquid. The results indicate that sheets prepared in these mediums would show very poor strength, even after beating.

It appears surprising that none of the organic liquids which exert a swelling effect upon the stearoylated fibers are capable of producing bonds between the ester groups of the individual fibers of sufficient strength to produce a coherent and strong sheet of paper. This result is in direct contrast to the very favorable effect of acetone upon partially acetylated fibers and must be the result of the hydrophobic properties of the stearoyl radical. The effect of acetone upon partially acetylated fibers may be regarded as
consisting of the solvation of ester groups which subsequently, as
the solvent is removed, approach each other closely so that their bond-
ing forces become operative. At the same time, unesterified hydroxyl
groups of adjacent fibers are probably drawn closely together so that
their bonding forces also come into play and complete the process of
bonding.

The swelling of the partially stearoylated fibers in certain
organic liquids seems to indicate that the stearoyl groups become
solvated. However, it would appear that, when the solvent is
evaporated, their length prevents the close approach which is re-
quired to make operative the bonding forces between stearoyl groups;
the unesterified hydroxyl groups are subject to the same effect. As
a result, very little or no bonding occurs. This interpretation appears
to be substantiated by the results reported by Hagedorn and Föller (9),
who found that the tensile strength of films prepared from cellulose
triacetate was 9-12 kg./sq. mm., whereas that of films from cellulose
tristearate amounted to only 0.5 kg./sq. mm.

HYDROSOCRIPCITY VALUES OBTAINED ON THE STEAROYLATED FILMS

Hygroscopicity measurements were made on the stearic acid
esters, using both the unbeaten and beaten materials. The results are
presented in Table XII. In Figures 9 and 10, the hygroscopicities of
the products at 30 per cent relative humidity (curve 2) are plotted
against the percentage of hydroxyl groups covered, as well as against
the stearoyl content (figures in brackets).
TABLE XIX

RESULTS OF HYDROSCOPICITY MEASUREMENTS of STEAROYLATED PULPS

<table>
<thead>
<tr>
<th>Apparent Stearoyl Content, %</th>
<th>Hydroxyl Groups Covered, %</th>
<th>Percentage Moisture at Various Humidities</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>60% R.H. 0-40 Min.</td>
</tr>
<tr>
<td>Unesterified material</td>
<td>-</td>
<td>9.6</td>
</tr>
<tr>
<td>15.8</td>
<td>4.1</td>
<td>7.3</td>
</tr>
<tr>
<td>32.3</td>
<td>10</td>
<td>4.5</td>
</tr>
<tr>
<td>42.6</td>
<td>15</td>
<td>4.0</td>
</tr>
<tr>
<td>51.5</td>
<td>21.7</td>
<td>2.9</td>
</tr>
<tr>
<td>60.2</td>
<td>30.7</td>
<td>3.9</td>
</tr>
</tbody>
</table>

*Note: Interval on unabated

**40-minute beating interval
From the data and the curves, it is seen that the hygroscopicity dropped rapidly as the stearyl content was increased. When the stearyl content of the pulp was 15.9 per cent (4.1 per cent of the hydroxyl groups covered), the hygroscopicity was found to be 13 plus. It fell to between 5 and 6 per cent when 20 to 30 per cent of the hydroxyl groups were replaced by stearyl groups. In the case of the acetates, about 13 per cent of acetyl (corresponding to 37.4 per cent of the hydroxyl groups covered) were required to reduce the hygroscopicity to approximately the same value. Thus, it is seen that the long chain stearyl acid molecule is more effective than the acetyl group in reducing the moisture retained by the fibers at any given relative humidity, regardless of whether the comparison is made on the basis of the weight of acyl introduced or on that of the percentage of hydroxyl groups replaced. However, the comparison on the basis of the percentage of hydroxyl groups replaced shows the effect of the longer chain acid radical more advantageously, because a replacement of 4.1 per cent of the hydroxyl groups causes approximately the same reduction in hygroscopicity as a replacement of 27.6 per cent of the hydroxyl groups by the acetyl group.

Comparison of curves 2 with curves 1 in Figures 9 and 10 shows that a direct relationship exists between the water-binding properties and the physical strength characteristics of the sheets prepared from the partially stearoylated fibers. This is similar to the relations shown by Aiken and by the present investigation to exist for the acetylated materials, with the exception of an initial increase. However, the strength properties seemed to fall off more
rapidly than the hygroscopicity. The explanation for this exception given above may be expanded with the following postulation. The introduction of very small amounts of stearoyl (less than 1.4 per cent replacement of the hydroxyl groups of cellulose) would make the material sufficiently hydrophobic to prevent the occurrence of increased hygroscopicity, in spite of a greater distance between adjacent cellulose chains which could be expected to result from the introduction of the much longer stearoyl radicals in comparison with the shorter acetyl radical.

HYGROEXPANSIVITY MEASUREMENTS ON THE STEAROYLATED PULPS

Hygroexpansivity measurements were made on the sheets prepared from the partially stearoylated pulps, a summary of which is given in Table XIII. The changes in hygroexpansivity with a relative humidity change of from 10 to 30 per cent (curves 3) are plotted against the stearoyl content and other characteristics in Figures 7 and 10.

The hygroexpansivity was greatly reduced as the stearoyl content was increased. This reduction was between 70 and 75 per cent when 20 to 30 per cent of the hydroxyl groups were covered (15 to 60 per cent stearoyl content). However, this decrease may have been partially due to the low coherent density of the sheets, which would have allowed the individual fibers to expand without causing an over-all change in the sheet as would be found with a sheet having a high coherent density. Approximately the same reduction (55 to 60 per cent) was shown by both the unbeaten and the beaten material containing 42.6 per cent stearoyl. The coherent densities were 5.6 and
TABLE XI  

EFFECT OF HUMIDITY CHANGES UPON THE PERCENTAGE CHANGE IN LENGTH OF HANDSHEETS

<table>
<thead>
<tr>
<th>Apparent Hydroxyl Stearoyl Groups</th>
<th>Humidity Change</th>
<th>Humidity Change</th>
<th>Humidity Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content, %</td>
<td>Covered, %</td>
<td>10% to 30% 0-40 min.</td>
<td>10% to 60% 0-40 min.</td>
</tr>
<tr>
<td>Unesterified Material</td>
<td>-</td>
<td>0.135</td>
<td>0.145</td>
</tr>
<tr>
<td>15.8</td>
<td>4.1</td>
<td>0.09</td>
<td>0.10</td>
</tr>
<tr>
<td>32.8</td>
<td>10.0</td>
<td>0.055</td>
<td>0.045</td>
</tr>
<tr>
<td>42.6</td>
<td>15</td>
<td>0.15</td>
<td>0.145</td>
</tr>
<tr>
<td>51.5</td>
<td>21.7</td>
<td>0.03</td>
<td>0.075</td>
</tr>
<tr>
<td>60.2</td>
<td>30.7</td>
<td>0.035</td>
<td>0.095</td>
</tr>
</tbody>
</table>

These intervals are unesterified

--0-minute-heating-interval

8.2, respectively. Thus, it may be concluded that the reduction in hygroexpansivity was caused by a decrease in the extension of the fibers and was not the result of changes in sheet formation, such as apparent density.

The interpretation of the data depends on whether the percentage of hydroxyl groups or the percentage of SO2 present are used.
When the hygroexpansivities of the stearoylated pulps are compared with those of the acetoylated pulps, it may be seen that a very much smaller percentage of hydroxyl groups needs to be replaced by stearoyl groups than by acetyl groups to bring about the same reduction in hygroexpansivity. However, if the hygroexpansivities of the esters are compared on the basis of the percentage of acyl groups present by weight, the comparison is in favor of the acetyl groups. For example, with an ester with a stearoyl content of 25 per cent (3 per cent of the hydroxyl groups replaced), the hygroexpansivity of the unbeaten sheets would be expected to be about 0.32 per cent; for an acetyl content of 25 per cent (42 per cent of the hydroxyl groups replaced), the value would be expected to be about 0.30 per cent.

Figures 9 and 10 also show that the direct relationship which was shown to exist at varying degrees of substitution between the physical strength characteristics, the water-binding properties, and the hygroexpansivities in the case of the acetates also holds for the stearoylated pulps.

In addition, it has been established that the esterification with a long carbon chain fatty acid requires the replacement of only a very small percentage of the hydroxyl groups of cellulose to produce a substantial reduction of the bonding forces, the water-binding properties, and the hygroexpansivities of the sheets prepared from these materials. The possibility of preparing a sheet with good strength properties from the stearates and thus making possible the practical use of the substantial reduction in hygroexpansivity was
found to be very remote because of the poor bonding forces exhibited on treatment of the esters with water or with organic liquids.

BUTYRATES

The butyryl radical was chosen as ranging between the extremes—the acetyl on the one hand and the stearyl on the other. Some information was available on the properties of cellulose butyrates which seemed to justify its choice. However, for the preparation of the butyrylated fibers in the present investigation, the usual methods which employ either butyryl chloride (26) or butyric anhydride in the presence of an acid catalyst (29) were not used to avoid degradation. Instead, the Vees and Sjubitsch method of acetylation was adapted to the butyrylation of Mitscherlich pulp—i.e., butyric anhydride was used in the presence of pyridine. As far as can be ascertained from the literature, this method is presented for the first time.

THE PREPARATION OF HYDROBUTYRATES OF VARIOUS DEGREES OF CONSTITUTION

The details of the esterification procedure were the same as those previously described for the acetylation, with the exception of the washing. The butyrylates were washed as follows: After the removal of the pulp from the constant temperature bath, they were filtered on a Buchner funnel and washed once with pyridine, three times with hot water, twice with recovered ethanol, twice with fresh ethanol and, finally, three times with ether. The pulps were dried in the air after the final ether wash.
The esterifications were carried out with fresh mixtures each time. The total butyrylation mixture, including the pyridine remaining in the pulp and, amounted to 16 ml. butyric anhydride and 16 ml. pyridine per gram of pulp. A few preliminary experiments with small pulp samples were made to determine the approximate rates and degrees of substitution at different temperatures.

Table XIV gives a summary of the conditions of butyrylation, the butyral contents obtained, the percentage of hydroxyl groups covered, and the degree of polymerization of the esters. The latter values were determined as described earlier—i.e., by dissolving the lignin in caustic soda solution at 20°C. and measuring the specific viscosities. While the material was dissolved, it became gelified; it was not necessary, therefore, to regenerate the cellulose constituent in a separate procedure and then prepare a solution of the regenerated cellulose in caustic soda solution.

But this technique was justified is shown by the results of the following experiment. A sample of the pulp containing 27.45 per cent butyral was regenerated with alcoholic alcohol in a nitrogen atmosphere (to avoid degradation) by a procedure similar to the one described by Hattinger for the regeneration of cellulose from its acetate. The regenerated material was then dissolved in caustic soda and the specific viscosity determined. The degree of polymerization of the regenerated cellulose calculated from the viscosity data was found to be 1501. The direct determination gave the value of 1500 (calculated on the cellulose content of the
### Table XIV

**Conditions of Butyrylation and Butyril Contents of Modified Pulps**

<table>
<thead>
<tr>
<th>Pyridine, ml./g. of Pulp</th>
<th>Butyric Anhydride, ml./g. of Pulp</th>
<th>Time, hr.</th>
<th>Temperature °C</th>
<th>Apparent Butyryl Content, %</th>
<th>Hydroxyl Groups Covered, %</th>
<th>Degree of Polymerization</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Preliminary Experiments</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>15</td>
<td>24</td>
<td>40</td>
<td>16.44</td>
<td>14.5</td>
<td>—</td>
</tr>
<tr>
<td>16</td>
<td>15</td>
<td>36</td>
<td>30</td>
<td>21.4</td>
<td>20.5</td>
<td>—</td>
</tr>
<tr>
<td><strong>Experimental Series</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Original Pulp</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>16.3</td>
</tr>
<tr>
<td>16</td>
<td>14</td>
<td>2</td>
<td>25</td>
<td>8.35</td>
<td>7.3</td>
<td>—</td>
</tr>
<tr>
<td>16</td>
<td>14</td>
<td>3</td>
<td>60</td>
<td>14.0</td>
<td>13.2</td>
<td>14.9</td>
</tr>
<tr>
<td>16</td>
<td>14</td>
<td>24</td>
<td>60</td>
<td>17.43</td>
<td>15.9</td>
<td>—</td>
</tr>
<tr>
<td>16</td>
<td>14</td>
<td>35</td>
<td>60</td>
<td>20.39</td>
<td>19.2</td>
<td>19.3</td>
</tr>
<tr>
<td>16</td>
<td>14</td>
<td>156</td>
<td>60</td>
<td>32.85</td>
<td>32.2</td>
<td>15.10</td>
</tr>
</tbody>
</table>
esterified pulp sample), indicating a very good agreement.

The data in Table XIV show that a series of butyrates with increasing butyryl content may be satisfactorily prepared by the Hess and Ljubitsch technique, the chief means of increasing the butyryl content being the time factor. The time required to reach the higher degrees of substitution was rather long. An inspection of the degree of polymerization shows that the cellulose had suffered some degradation. However, the decrease in degree of polymerization (about 10 percent) is so small that it probably would not influence the physical properties of the sheets prepared from the materials to a noticeable extent.

PHYSICAL STRENGTH PROPERTIES OF SHEETS PREPARED FROM THE BUTYRALATED PULPS

The strength properties of the butyralated pulps were evaluated at the zero and 40-minute beating intervals. The results are given in Tables XV and XVI. The data in Table XVI are calculated on the original cellulose basis. The figures show that the butyrates processed in water suffer a sharp decrease in all strength properties as the degree of substitution increases. To illustrate this further, the bursting strength values, being most typical of the strength characteristics, were plotted against the percentage of hydroxyl groups covered and the butyryl content. The results are shown in Figure A1 for the unbeaten material, and in Figure A2 for the beaten materials. From the data and curves, it can be seen that the strength properties were practically negligible after a butyryl content of between 17 and
<table>
<thead>
<tr>
<th>Butyryl Content, %</th>
<th>Hydroxyl Covered, %</th>
<th>Basis Weight</th>
<th>Density</th>
<th>Apparent Burst Factor</th>
<th>Tear Factor</th>
<th>Tensile Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unbeaten - Water medium</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unesterified pulp</td>
<td>4.2</td>
<td>43.4</td>
<td>10.1</td>
<td>16.2</td>
<td>2.63</td>
<td>11.2</td>
</tr>
<tr>
<td>8.36</td>
<td>7.3</td>
<td>4.1</td>
<td>42.9</td>
<td>10.45</td>
<td>7.9</td>
<td>10.2</td>
</tr>
<tr>
<td>14.0</td>
<td>12.2</td>
<td>5.6</td>
<td>46.9</td>
<td>3.4</td>
<td>11.5</td>
<td>1.0</td>
</tr>
<tr>
<td>17.45</td>
<td>15.0</td>
<td>7.6</td>
<td>55.0</td>
<td>7.2</td>
<td>7.8</td>
<td>0.71</td>
</tr>
<tr>
<td>20.35</td>
<td>19.2</td>
<td>8.1</td>
<td>51.1</td>
<td>6.7</td>
<td>6.1</td>
<td>0.44</td>
</tr>
<tr>
<td>22.95</td>
<td>23.2</td>
<td>3.26</td>
<td>57.1</td>
<td>6.2</td>
<td>3.5</td>
<td>0.32</td>
</tr>
</tbody>
</table>

Beaten for 40 minutes in-water-in-the-steam-kiln

| Unesterified pulp | 2.7 | 43.5 | 16.3 | 161.0 | 0.9 | 51.5 |
| 8.36 | 7.8 | 2.7 | 43.7 | 16.2 | 131.5 | 0.9 | 49.0 |
| 14.0 | 12.2 | 3.4 | 43.1 | 14.2 | 39.5 | 0.8 | 19.1 |
| 17.45 | 16.0 | 5.2 | 54.5 | 10.5 | 13.4 | 1.24 | 7.0 |
| 20.35 | 19.2 | 5.0 | 53.7 | 10.7 | 7.5 | 0.23 | 3.9 |
| 22.95 | 23.2 | 5.4 | 56.0 | 10.3 | 4.7 | 0.17 | 1.8 |

Beaten for 40 minutes in-the-steam-kiln

| Acetone medium |
|-----------------|--------------|-----|-----|-------|-------|
| 22.95 | 23.2 | 5.0 | 53.6 | 11.7 | 49.9 | 1.36 | 13.0 |

10% Acetone medium

| 20.35 | 19.2 | 4.8 | 58.1 | 12.3 | 4.3 | 0.32 | 2.8 |

5% Sarcosine-water emulsion

| 20.35 | 19.2 | 4.7 | 50.7 | 10.7 | 30.5 | 0.70 | 11.2 |
### TABLE XVI

**PHYSICAL STRENGTH PROPERTIES OF SHEETS PREPARED FROM BUTYLATED ULS**

*(Calculated on Cellulose Basis)*

<table>
<thead>
<tr>
<th>Apparent Hydroxyl Butyryl Groups Content, Covered, %</th>
<th>Basis Caliper Weight Density Factor</th>
<th>Apparent Burst Factor</th>
<th>Tear Factor</th>
<th>Tensile Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Unbeaten</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unesterified pulp</td>
<td>4.2</td>
<td>43.3</td>
<td>10.1</td>
<td>26.2</td>
</tr>
<tr>
<td>8.36</td>
<td>7.3</td>
<td>4.1</td>
<td>39.4</td>
<td>9.6</td>
</tr>
<tr>
<td>14.0</td>
<td>12.2</td>
<td>5.6</td>
<td>40.3</td>
<td>7.24</td>
</tr>
<tr>
<td>17.95</td>
<td>16.0</td>
<td>7.6</td>
<td>45.5</td>
<td>5.36</td>
</tr>
<tr>
<td>20.35</td>
<td>19.2</td>
<td>8.1</td>
<td>44.2</td>
<td>5.4</td>
</tr>
<tr>
<td>22.95</td>
<td>22.2</td>
<td>9.3</td>
<td>44.2</td>
<td>4.8</td>
</tr>
<tr>
<td><strong>Beaten for 40 Minutes in the Lamken Mill</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unesterified pulp</td>
<td>3.66</td>
<td>43.5</td>
<td>16.3</td>
<td>161.0</td>
</tr>
<tr>
<td>8.36</td>
<td>7.3</td>
<td>2.7</td>
<td>40.1</td>
<td>14.85</td>
</tr>
<tr>
<td>14.0</td>
<td>12.2</td>
<td>3.4</td>
<td>41.5</td>
<td>12.2</td>
</tr>
<tr>
<td>17.95</td>
<td>16.0</td>
<td>5.2</td>
<td>45.1</td>
<td>3.7</td>
</tr>
<tr>
<td>20.35</td>
<td>19.2</td>
<td>5.0</td>
<td>42.9</td>
<td>8.56</td>
</tr>
<tr>
<td>22.95</td>
<td>22.2</td>
<td>5.4</td>
<td>43.0</td>
<td>8.0</td>
</tr>
<tr>
<td><strong>Beaten for 40 Minutes in the Lamken Mill</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### Acetone Medium

| 22.95                                                | 22.2                               | 5.0                  | 45.6        | 3.0           | 40.0          | 2.4         | 16.3        |

#### 10% Acetone Medium

| 20.35                                                | 19.2                               | 4.8                  | 43.3        | 9.3           | 10.4          | 0.41        | 6.0         |

#### 5% Benzene–Water Emulsion

| 20.35                                                | 19.2                               | 4.7                  | 40.1        | 8.5           | 38.2          | 1.13        | 14.7        |
21 per cent had been reached, corresponding to a replacement of between 15 and 19 per cent of the hydroxyl groups. The butyrylated pulp with the lower degrees of substitution showed good strength development when beaten in water. For example, the handsheets prepared from the material containing 9.36 per cent butyryl had a bursting strength of 27.2 at the zero interval and 131.5 at the 40-minute interval. However, the higher the butyryl content, the closer the strength values for the unbeaten and the beaten materials approach each other.

If the strength properties of the acetates and the butyrylates are compared, it can be seen that the presence of between 17 and 21 per cent butyryl content (15 to 19 per cent of the hydroxyl groups replaced) had about the same effect on the strength properties as 30 to 35 per cent acetyl content (30 to 45 per cent of the hydroxyl groups replaced). Thus, it may be said that the hydrophilic character and hydrating characteristics of cellulose were reduced to a greater extent by replacing the hydroxyl groups with butyryl groups than by replacing them with acetyl groups, or that with butyrylation a lower degree of substitution sufficed to produce a result equivalent to that obtained with acetylation.

It should be added that the physical strength properties of the butyrylated pulps did not show the maximum in the lower stages of substitution, as was observed with the acetylated fibers. It could never be explained as the assumption that the critical lower ranges of substitution had been missed. In other words, it is possible that the maximum would have been observed, if the degree of
substitution had been kept below a butyryl content of 3.35 per cent - 

i.e., the lowest-substituted product used in this investigation.

Curve 1 in Figure 11 seems to indicate the tendency between zero 

and about 9 per cent butyryl, the final point of the curve.

Microscopic observations of the beaten pulp demonstrated 

that the butyryls with the higher degrees of substitution and very 

low strength properties had been crushed and broken during the beating 

operation. The fibers had the same appearance as the beaten acetates 

and acetates of the higher degrees of substitution. 

In Table 2, some of the data obtained during the beating 

tests, for instance, are given in a 5 per cent butyryl pulp, and 

equivalent beating time experiments were made with acetone. 

mediums—other than water. The test results of the handsheets from 

these experiments are also given in Tables XV and XVI. The material 

containing 22.95 per cent of butyryl had a bursting strength of 32.93

when beaten for 40 minutes in acetone, as compared with 4.7 when 

beaten for the same time in water; this is quite a remarkable improve- 

ment and demonstrates the beneficial influence of acetone as a 

beating medium for the butyrylated pulp. The material containing 20.35

per cent of butyryl showed a bursting strength of 4.4 when beaten for 

60 minutes in 10 per cent aqueous acetone, and of 30.5 when beaten 

for the same time in a 5 per cent benzene-water emulsion, as com- 

pared with 7.8 when processed for an equivalent time in water. The 

5 per cent benzene-water emulsion was prepared by stirring approxi- 

mately equal parts of benzene and water for 5 minutes in a Waring blender. 

A small percentage of alpha protein (0.01 per cent) was added to 

stabilise the emulsion. The water necessary to give a 5 per cent
benzene-water emulsion was then added, with very vigorous stirring. The butyrylated pulp, when processed in the emulsion, became very "slow,"—i.e., a long time was required for draining the stock. It is interesting to note that the strength properties of the material beaten in the emulsion were almost as good as those of the material beaten in acetone.

Hygroscopicity of Sheets Prepared from the Butyrylated Fibers

Hygroscopicity measurements were made on the butyrate sheets beaten in water at the zero and 95-minute intervals, the results of which are presented in Table XX. The values for the hygroscopicity at 90% relative humidity which were typical of the results are plotted in Figures 11 and 12 (curve 2) against the percentage of hydroxyl groups covered. The butyryl contents are given in brackets.

From the data and curves, it is apparent that the hygroscopicity of the butyrylated pulp decreased after the first few percentage of butyryl had been introduced. The beaten material showed a slightly higher hygroscopicity than the unbeaten material for the corresponding butyryl content. This slight difference may possibly be attributed to the opening up of the structure on beating, thus making more hydroxyl groups accessible for hydration and absorption. The hygroscopicity of the unbeaten pulp decreased from 18.6 per cent for the unesterified material (at 90% relative humidity) to 6.1 per cent, when 27.2 per cent of the hydroxyl groups of the cellulose were covered (butyryl content of 27.95 per cent).


### Hygroscopicity of Butylated Acids

<table>
<thead>
<tr>
<th>Butyryl Content, %</th>
<th>Hydroxyl Groups Covered, %</th>
<th>0.62-in.</th>
<th>0.1-in.</th>
<th>0.14-in.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unbutyrylated material</td>
<td>9.6</td>
<td>9.4</td>
<td>12.8</td>
<td>13.4</td>
</tr>
<tr>
<td>8.36</td>
<td>7.3</td>
<td>3.4</td>
<td>9.1</td>
<td>11.2</td>
</tr>
<tr>
<td>14.0</td>
<td>12.2</td>
<td>6.2</td>
<td>7.2</td>
<td>3.9</td>
</tr>
<tr>
<td>17.45</td>
<td>16.0</td>
<td>5.1</td>
<td>5.6</td>
<td>7.3</td>
</tr>
<tr>
<td>20.95</td>
<td>19.2</td>
<td>4.4</td>
<td>4.8</td>
<td>6.9</td>
</tr>
<tr>
<td>22.95</td>
<td>22.2</td>
<td>3.2</td>
<td>4.1</td>
<td>4.5</td>
</tr>
</tbody>
</table>

*Note: 40-minute-heating interval.*

The beaten materials showed a decrease in hygroscopicity of from 13.3 to 8.2 per cent over the same range.

As seen from Figures 11 and 12, the hygroscopicities followed fairly closely the bursting strength values in much the same way as was shown for the acetates and the acetates.

**Hydroexpansivity of Butylated Acids**

Hydroexpansivity measurements were made on the unbeaten and beaten materials, previously-formed into bond sheets. The results are
presented in Table XVII. The hydroexpansivities for a humidity change of from 10 to 30 per cent were also plotted against the percentage of hydroxyl groups covered (and butyryl contents) and the results are shown in Figures 11 and 12.

It is seen from the data in Table XVII that the hydroexpansivity of the material with 33.95 per cent butyryl had decreased by about 62 per cent for the unbeaten and by 67 per cent for the beaten material (relative humidity change of from 10 to 30 per cent). In spite of these differences in the apparent densities, the beaten and unbeaten materials had approximately the same hydroexpansivity for a given change in relative humidity.

If the reduction in hydroexpansivity, as shown by the butyrylates, is compared with that which was obtained with the acetates, it becomes apparent that the butyryl group is considerably more efficient than the acetyl group. For example, a butyryl content of 29.35 per cent (19.0 per cent of the hydroxyl groups covered) reduced the hydroexpansivity by about 53 per cent, whereas an acetyl content of 25.65 per cent (13 per cent of the hydroxyl groups covered) reduced this property only by about 40 per cent (relative humidity change of from 10 to 30 per cent).

Figures 11 and 12 show that, as could have been expected, the hydroexpansivities are in direct relationship with the physical strength properties and hydroexpansivities, in much the same way as was observed with the acetates and butyrylates.
### TABLE VII

**HYDROEXPANSIVITY OF SHEETS PREPARED FROM METHYLATED PULPS**

**Absorption-Cycle**

<table>
<thead>
<tr>
<th>Percent Hydroxyl Butyryl Groups Covered, %</th>
<th>Humidity Change</th>
<th>Humidity Change</th>
<th>Humidity Change</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>17% to 30% 40-Min.</td>
<td>10% to 60% 40-Min.</td>
<td>10% to 30% 40-Min.</td>
</tr>
<tr>
<td>Unesterified Material</td>
<td>0.13</td>
<td>0.145</td>
<td>0.115</td>
</tr>
<tr>
<td></td>
<td>0.35</td>
<td>0.465</td>
<td>0.52</td>
</tr>
<tr>
<td>8.36 7.8</td>
<td>0.09</td>
<td>0.10</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>0.295</td>
<td>0.48</td>
<td>0.45</td>
</tr>
<tr>
<td>14.0 12.2</td>
<td>0.355</td>
<td>0.075</td>
<td>0.205</td>
</tr>
<tr>
<td></td>
<td>0.255</td>
<td>0.345</td>
<td>0.42</td>
</tr>
<tr>
<td>17.45 16</td>
<td>0.04</td>
<td>0.045</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>0.135</td>
<td>0.28</td>
<td>0.22</td>
</tr>
<tr>
<td>20.35 19.2</td>
<td>0.04</td>
<td>0.04</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>0.13</td>
<td>0.225</td>
<td>0.215</td>
</tr>
<tr>
<td>22.35 22.2</td>
<td>0.03</td>
<td>0.03</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>0.175</td>
<td>0.17</td>
</tr>
</tbody>
</table>

---

*Zero interval or unbeaten*

++ 40-minute beating interval

The remarkable reduction in hygroexpansivity which may be obtained by treatment with the introduction of a limited amount of butyryl is worth attention, as it is considered that such a reduction may be combined with fair physical strength properties by treating the butyrylated material in acetone or benzene (or possibly other relatively sheer emulsions).
1. A series of partially acetylated fibers was prepared from bleached Mitscherlich pulp with acetic anhydride and pyridine at temperatures of 24° and 40° C., following the method of Hess and Ljubitsch as modified by Aletzinger. The acetyl contents of the 13 preparations ranged from 3.5 to 35.65 per cent, and in most cases did not differ by more than 2 to 3 per cent.

The possibility of increasing the rather slow rate of reaction of the Hess and Ljubitsch method was studied by using temperatures of 60° to 80° C. At these higher temperatures the rate of reaction was considerably increased without degrading the cellulose to any appreciable extent. The use of acetyl chloride in pyridine was also investigated. At a temperature of 80° C., the rate of acetylation was increased but the cellulose was somewhat more degraded than with acetic anhydride. Acetic anhydride at the higher temperatures gave more rapid rates of acetylation than acetyl chloride at 24° C. and with less degradation.

2. Sheets were prepared from the series of partially acetylated fibers (1) by merely disintegrating them (in the British disintegrator) and (2) by beating them (in the Jenson mill) in water according to standard procedures. The sheets were tested for strength and other physical properties. The strength properties were found to increase with increasing acetyl content and to reach a maximum at an
acetol content of between 2 and 3 per cent. The physical strength properties decreased with a further increase in the degree of substitution until, at 25.65 per cent, they had almost disappeared. The maxima in the physical strength properties were more pronounced with the beaten than with the unbeaten materials. Microscopic observations showed that the more highly acetylated fibers, when beaten in water, were broken rather than fibrillated.

3. The hygroscopicities were determined according to standard procedures on "unbeaten" and "beaten" sheets. Both the absorption and desorption values were determined. The hygroscopicity increased and reached a maximum as the acetol content reached values ranging between 2.5 and 3 per cent. Thereafter, the hygroscopicities fell off rather rapidly. The trend of the hygroscopicity thus followed rather closely the trends of the physical strength properties. The lowest hygroscopicity for the unbeaten acetylated material of 25.65 per cent acetol content was 10.6 per cent (at 90 per cent relative humidity), a decrease of about 10 per cent. For the beaten material, the lowest hygroscopicity was 1.7 per cent or a decrease of about 34 per cent.

Although there were some irregularities, the hygroscopicity curves showed the beaten materials to have somewhat higher hygroscopicity values than the unbeaten materials. The differences were more pronounced with the highest acetol contents (18.1 and 25.6 per cent).

4. The hygroexpansivity was determined in the Jeenah Expansimeter. It was found that the hygroexpansivity first increased and reached a maximum at an acetol content of from 2 to 6 per cent, which
is close to the range within which the maxima in hygroexpansivity and physical strength properties occurred. The hygroexpansivity then fell and followed closely the drop in the other two sheet characteristics as the acetyl content approached its highest value (25.6 per cent).

The maximum reduction in hygroexpansivity was from 0.465 per cent (the original value of the unacetylated material) to 0.30 per cent (the value of the 25.65 per cent acetyl content material) or a decrease of about 35 per cent for the unbeaten materials. The relation between the three sheet characteristics was not as close for the beaten materials, but the greatest reduction was from 0.52 per cent (unacetylated material) to 0.265 per cent (material containing 25.65 per cent acetyl), or a decrease of about 50 per cent. The indications were that the sorption density did not enter as an essential factor to account for the difference in hygroexpansivities between the acetylated and the unacetylated materials.

5. The lack of physical strength properties encountered with the sheets when they showed their highest reduction in hygroexpansivity could be partially eliminated by beating the acetylated material in acetone and preparing the sheets from the acetone suspension. Thus, sheets were obtained which combined reduced hygroexpansivity with good physical strength properties. The reduction in hygroexpansivity in these experiments amounted to 28.7 per cent for the unbeaten and 33 per cent for the beaten sheets.

6. Microscopic observations showed that the acetylated
fibers, when beaten in acetone, were not unduly broken; on the contrary, they appeared fibrillated and brushed out at the ends in much the same way as unacetylated fibers after beating in water.

STEARATES

1. For studying the effect of esterification with higher fatty acids upon the three sheet characteristics—physical strength properties, hygroscopicity, and hydroexpansivity—samples of the Mitscherlich pulp were subjected to partial stearoylation. The method used was a modification of that of Grän and Wittka (27), employing stearoyl chloride in the presence of pyridine as the neutralizing and swelling agent and benzene as a diluent. The temperature was kept below 40°C. By varying the time from a few to 67 hours, a series of six partially stearoylated fiber preparations was obtained, ranging from 15.3 to 60.2 per cent stearoyl. The latter value corresponded to a substitution of slightly less than 1 stearoyl group per anhydro-glucose unit.

Difficulties were encountered in determining the degree of substitution by the method suggested by Comyn and Bellat (11), which consists of the saponification of the stearate with alcoholic sodium hydroxide and titration of the excess alkali. The stearoyl content values were generally too high. This was demonstrated by checking the values through elementary analysis. In view of the fact that the latter method also lacks reliability if the degree of substitution is low, recourse was made to the direct isolation of the stearic acid liberated from the stearate by saponification and sub-
sequent acidification. Good checks were obtained with this method.

Further difficulties were encountered in determining the degree of polymerization of the stearates, using the method of measuring the specific viscosities in cuprammonium hydroxide and converting the viscosity data into the average degrees of polymerization by Steudinger's equation. The stearates did not dissolve in cuprammonium hydroxide solution. Various treatments and modifications had no effect on the solubility. In addition, it was found that the cellulose regenerated from the stearate by saponification (using a procedure similar to that described above) did not dissolve in cuprammonium hydroxide. Because of these difficulties, the degree of polymerization of the stearoylated materials was not determined. Therefore, the evidence that the process of stearoylation does not unduly degrade the cellulose is based upon the appearance of the fibers, the rather mild conditions of stearoylation, and the insolubility of the stearates in the various solvents. This evidence appears quite convincing, although it is of an indirect nature.

2. The physical strength properties, the hygroscopicities, and the hydroexpansivities were determined on sheets prepared from the five stearoylated materials, and the values were compared with those obtained with the acetylated materials. It was found that the introduction of 15.2 per cent of stearoyl (which corresponds to a replacement of only about 4 per cent of the hydroxyl groups available in cellulose for esterification) sufficed to deprive the sheets of almost all their physical strength properties. It also caused the sheets to
be bulky (low apparent density) and strongly hydrophobic. With higher stearoyl contents, the fibers acquired a fatty feel, and the physical strength properties dropped still further. There was no increase in physical strength properties with the lower degrees of substitution, as was observed with the acetylated fibers. Very little strength development resulted from heating.

The hygroscopicity of the sheets from the stearoylated fibers dropped as the stearoyl content increased, but at a slower rate than the physical strength properties. In other words, at 12.8 per cent stearoyl content, where the physical strength properties were almost lost, the hygroscopicity was still 13 per cent. Only when 50 to 60 per cent of stearoyl had been introduced (corresponding to a replacement of 70 to 80 per cent of the available hydroxyl groups) did the hygroscopicity drop to as low a value as 4 to 5 per cent. The lowest hygroscopicity obtained with sheet from the acetylated materials was 10.5 per cent (at 90 per cent relative humidity), at an acetyl content of 29.65 per cent (corresponding to a replacement of 43 per cent of the hydroxyl groups). The stearates did not show an initial increase (or a maximum) in the hygroscopicity at the lower degrees of substitution.

The hygroexpansivity of the sheets was greatly reduced as the stearoyl content increased but, again, the reduction took place at a somewhat slower rate than the drop in physical strength properties. At a stearoyl content of 12.8 per cent, the reduction was from 0.465 per cent (unbeaten, unsterified material) to 0.42 per cent, or a de-
crease of about 9.5 per cent. Only when 50 to 60 per cent stearoyl had been introduced (corresponding to a replacement of 23 to 30 per cent of the hydroxyl groups) did the hydroxensivity fall to 0.115 and 0.145, corresponding to a reduction of 69 to 75 per cent.

Compared with the effect of acetylation, it was shown that both an acetyl content and a stearoyl content of 25 per cent reduced the hydroxensivity to about the same value (0.32 to 0.36 per cent, respectively); however, the 25 per cent acetyl content corresponded to a replacement of about 42 per cent of the hydroxyl groups, whereas the 25 per cent stearoyl content corresponded to approximately 2 per cent replacement.

Attempts to increase the physical strength properties of the hand sheets by processing the stearoylated fibers in an organic liquid instead of in water were unsuccessful, although a number of the organic liquids tried had a distinct swelling effect upon the stearoylated fibers.

BUTYRATES

1. Butyryl was chosen as a radical intermediate between the stearoyl and the acetyl. It was introduced into the Kotscherlich pulp by subjecting the fibers to the action of butyric subhydride in pyridine at 60°C for varying lengths of time. As far as could be ascertained, this method had not been employed before for the preparation of the butyres of cellulose. The rate of reaction was slow; 256 hours being required to introduce 22.25 per cent butyryl. The lowest product had 2.36 per cent butyryl and was obtained after allowing the reaction
to proceed at 25°C for 2 hours. A series of five preparations of increasing butyryl content was prepared.

2. No difficulties were encountered in dissolving the butyrates in copperammonium hydroxide and thus determining the degree of polymerization directly. Under the conditions employed, the cellulose had been only slightly degraded. The degree of polymerization decreased from 1653 to an average of 1493, or 160 points (amounting to less than 10 per cent).

3. The three sheet characteristics were determined on sheets prepared from the unbeaten and beaten butyrylated pulp. The physical strength properties, the hygroscopicity, and the hydroexpansivity of the sheets all decreased with increasing butyryl content. No initial increase or development of a maximum was observed. The strength properties became practically zero after 17 to 19 per cent butyryl had been introduced, corresponding to a replacement of between 15 and 19 per cent of the hydroxyl groups. At these butyryl contents, the hygroscopicity was still between 9.5 and 7.7 per cent for the unbeaten and 11.2 and 9.6 per cent for the beaten materials. Even when 22.95 per cent butyryl had been introduced (corresponding to a replacement of 22.2 per cent of the hydroxyl groups), the hygroscopicities were still 6.1 per cent for the unbeaten and 3.3 per cent for the beaten material. At that butyryl content at which the physical strength properties became practically zero, the hydroexpansivity was between 0.23 and 0.225 per cent for the unbeaten and between 0.25 and 0.015 for the beaten material (over a relative humidity change of from 10 to
80 per cent). At the highest butyryl content (22.95 per cent), the hydroexpansivity was 0.175 per cent for the unbeaten material and 0.17 per cent for the beaten material, corresponding to reductions from the unesterified sheets of approximately 62 and 67 per cent, respectively.

4. The lack of physical strength encountered in sheets prepared from butyrylated fibers disintegrated or beaten in water was partially eliminated by beating them in acetone. These sheets had fairly good physical strength properties. It was also shown that, instead of acetone, an emulsion of a relatively small amount of benzene (5 per cent) in water could be used as a processing medium for the beating and sheetmaking, with similar results in physical strength properties.

DISCUSSION OF RESULTS

The physical strength characteristics, the hygroscopicities, and the hydroexpansivities of the acetates, butyrates, and stearates were compared in Figures 13, 14, 15, 16, 17, and 18. These curves were plotted with the various properties as the ordinates and the percentage of hydroxyl groups replaced by acyl groups as the abscissae. Comparisons for both the unbeaten and the beaten materials are presented.

From these figures, it is apparent that, at any given degree of substitution, the various properties are reduced in accordance with the number of carbon atoms present in the acyl group. Thus, it is
Figure 13

Effect of Reduced Capacity on Bursting Strength of Treated Films

Percentage of Hydroxyl Groups Replaced by Acyl Groups vs. Bursting Strength (lb. in. per 100 ft.)

Curves:
1. Lactate
2. Palmitate
3. Stearate
Percentage of hydroxyl groups replaced by acyl groups
Figure 15

Hydroxyl Content of the P19 Methyl Ester

Saponification Interval
Acid Formation Index
Relative Stability

Curve 1 A  
Curve 2 Intermate 
Curve 3 Stearate

Percentage of Hydroxyl GROUP Replaced by Acyl Groups
FIGURE 16

HYDROLYSIS OF AMINO ACIDS

No Limitation Interval

Experimental Data:

Relative Humidity 70%

Curve 1: Acetate
Curve 2: Butyrate
Curve 3: Stearate

Percentage of Molar Ratio Replaced by Acid Molar Ratio

Percentage of Molar Ratio Replaced by Acid Molar Ratio
Figure 17

Hydroxyl group content

Impinging interval

Absorption rate

Density change - 10% to 40%

Curve 1: acetyl
Curve 2: nitrate
Curve 3: stearate

Percentage of hydroxyl groups replaced by other groups
Figure 18

Hydroxyl Activity of AT-2835 Oils

No Plate Heating Interval

Absorption Data

Rimmy Change: 10% to 50%

Curve 1: Acetate
Curve 2: Butyrate
Curve 3: Stearate

Percentage Change in Length

Percentage of Hydroxyl Groups Replaced by methyl groups
seen that the acetyl group (CH₃CO) has a very much smaller effect on
the various properties than the butyryl (CH₃CH₂CO) and the stearoyl
groups (C₁₇H₃₅CO).

A comparison of the different properties at the various
degrees of substitutions shows that the stearoyl group appears to be
the most effective in reducing the water-binding and expansion proper-
ties. However, it should be observed that the physical strength
properties are practically eliminated when as little as ½ per cent of
the hydroxyl groups are covered, whereas the hygroscopicity and
hygroexpansivity are still high. Thus, it would appear that a very
low degree of substitution by the very long chain acyl radical imparts
sufficient of its highly hydrophobic characteristics to the cellulose
fibers to prevent the sheet from having any appreciable fiber-to-
fiber bonding. However, the remaining hydroxyl groups are still ef-
fective in absorbing a certain quantity of water and thus in causing
a certain hygroexpansivity. In order to create an appreciable reduc-
tion in the water-binding and expansion properties, more than 15 per
cent of the hydroxyl groups must be covered by stearoyl groups—i.e.,
a stearoyl content of above 35 per cent by weight must be present.

The pronounced effect of the stearoyl radical upon the
physical strength properties seems to be explained by the substantial
weight of this acyl radical which, in the lowest substituted prepara-
tion, amounts to 15 to 16 per cent of the weight of the fibers. In
addition, it may be postulated that the stearoyl chains are too long
to enter the spaces between adjacent cellulose chain molecules in a
rectangular position. Thus, they may be bent downward and arranged in a direction parallel to the cellulose chains. In this way, a very small percentage replacement of the available hydroxyl groups would cover a relatively great area of cellulose chains. But it may be assumed that, in spite of the bent position of the stearoyl chains, the distances between adjacent cellulose chain molecules are still so great that the free hydroxyl groups of the stearoylated fibers are unable to approach each other closely enough for intimate bonding, when the water is removed after the processing. This would perhaps explain the impossibility of preparing a coherent sheet of even modest strength properties from the lowest substituted fibers. Possibly, the same hypothesis may explain the failure of the stearoylated fibers to develop physical strength when treated with certain organic liquids.

These liquids appeared to exert a swelling effect upon the stearoylated fibers and thus may be assumed to solvate the stearoyl groups. In spite of this swelling, the cellulose chains remain too far apart when the organic liquid is removed to allow good bonding. This result is in contrast to the effect of acetone upon acetylated fibers. The acetyl groups are so short that the close contacts between adjacent cellulose chains required for intimate bonding do not seem to be impeded.

The butyrates follow the same trend as the stearates, but 5 to 10 per cent more hydroxyl groups must be covered to obtain the same reductions in properties. However, if the weights of the acyl groups are considered, it is seen that, with between 30 and 35 per cent acyl content by weight, the same reductions in water-binding and expansion properties are realized for the butyrates as with 30 to 40 per cent
acyl content for the stearate.

When the curves for the acetates and butyrates are compared, it is observed that, although very substantial decreases in hygroscopicity and hygroexpansivity occurred when 43 per cent of the hydroxyl groups of the cellulose were covered by acetyl groups (25.65 per cent acetyl content), these decreases do not equal those which may be realized with a butyrate in which 22.2 per cent of the hydroxyl groups are covered (22.95 per cent butyryl content). However, it must be recalled that the physical strength properties also show corresponding decreases.

The various comparisons seem to indicate that the acid radical having a carbon chain length intermediate between the two extremes—i.e., the butyryl—is the most effective of those used in changing the various sheet characteristics. This would suggest that the addition of only two CH₂ groups to the acetyl chain (CH₃CO⁻ → CH₃CH₂CH₂CO⁻), or possibly only one CH₂ group (as in the propionyl radical), has a much greater effect than would be anticipated. Thus, it would appear that, by adding more than two CH₂ groups to the acyl chain, the effect produced per CH₂ group would be only slightly increased. In other words, the effects of the fatty acid radicals between the butyryl and the stearoyl may all be expected to be within rather close range of each other. The similarity of the butyrylated and the stearoylated pulps gives the former a favorable position, if a commercial utilization of the reduction in hygroscopicity and hygroexpansivity is contemplated. Substantial physical strength properties may be obtained.
and made useful if acetone or hydrocarbon-water emulsions are used as heating and sheathing media for the butyrates.

The fact that, with the lower substituted stearylated and butyrylated materials, no maxima in physical strength properties, hygroscopicities, and hygroexpansivities were observed, as with the acetates, may be explained by assuming that even the lowest degrees of substitution were not low enough. Thus, the critical ranges were not obtained. On the other hand, it is possible that, even with such lower degrees of substitution than employed in this investigation, the strongly hydrophobic character imparted by the stearyl and butyryl radicals would predominate. A decision between these two possibilities can be made only by studying the effect of esterification at degrees of substitution below those employed in the present study.
SUBJECT

1. Fibrous cellulose esters of acetic, stearic, and butyric acids with varying degrees of substitution were prepared by mild esterification of bleached Mitscherlich pulp. The physical strength properties, hygroscopicities, and hygroexpansivities of sheets prepared from these fibers were studied.

2. From the experimental data and results on the acetylated fibers, the following conclusions can be drawn:

a. The rate of acetylation under the action of acetic anhydride was shown to be substantially increased by allowing the reaction to take place at elevated temperatures. The degradation of the cellulose at these temperatures was relatively small.

b. The superiority of the Hess and Ljubitash method for preparing undegraded, partially substituted esters over the acetyl chloride (in pyridine) method was shown.

c. The physical strength properties of sheets prepared from acetylated Mitscherlich pulp showed an initial increase and subsequent decrease with increasing acetyl content. These results confirmed those of Bletzinger and Aiken and lend support to the proposed hypothesis regarding the role which the hydroxyl groups of cellulose play in the papermaking processes.

d. Maxima in physical strength properties were also observed with sheets prepared from acetylated fibers which had been
merely disintegrated and not actually beaten. This result supports the hypothesis that the mere enlargement of the distances between adjacent chain molecules by acetylation suffices to produce increased accessibility of hydroxyl groups and its effect upon hydration and bonding.

2. The acetylated fibers were shown to be broken during beating in water. This effect aids in explaining the lack of physical strength properties at an acetyl content high enough to exert a pronounced hydrophobic effect.

3. The hygroscopicities of sheets from unbeaten and beaten pulps were found to follow closely the trends of the physical strength properties. This relation seems to establish more firmly the soundness of the above hypothesis.

4. The hygroexpansivities were found to follow the same trend as the hygroscopicities and the physical strength properties. The relation was not as close for the beaten materials as for the unbeaten materials.

5. Acetone, as a beating and sheetmaking medium, produced sheets of fair to good physical strength properties. In addition, it was shown that, on beating in acetone, the acetylated fibers were somewhat fibrillated. This aids in explaining the beneficial effect of processing in acetone.

6. The sheets prepared from the acetone-processed acetylated fibers showed a substantial reduction in hygroexpansivity. As noted in
b. This was combined with reasonable physical strength properties.

3. From the experimental data and results on the stearoylated fibers the following conclusions are drawn:

a. The physical strength properties, hygroscopicities, and hygroexpansivities decreased rapidly with increasing stearoyl content. No initial rise (or maximum) was observed for any of these properties.

b. Attempts to increase the physical strength properties of the stearoylated pulp by processing in organic liquids were unsuccessful.

c. When the three sheet characteristics are compared on the basis of the percentage of hydroxyl groups replaced, the stearoyl group caused a greater effect than the acetyl or butyryl group.

4. From the experimental data and results on the butyrylated fibers, the following conclusions may be drawn:

a. The physical strength properties, hygroscopicities, and hygroexpansivities decreased rapidly with increasing butyryl content. No initial increase (or maximum) was observed for any of these properties.

b. Substantial reductions in hygroscopicity and hygroexpansivity were shown by the butyrylated sheets.

c. Sheets from butyrylated fibers processed in organic liquids (acetone and benzene-water solution) had fair strength properties.
4. Of the acyl radicals studied, the butyryl seemed to be the most effective (on the basis of the percentage of acyl content) in reducing the hygroscopicity and hygroexpansivity.

5. The effect upon the sheet characteristics increases with increasing chain length of the acid radical.

6. The desired reductions in hygroexpansivity and hygroscopicity were reached only when the physical strength properties had almost disappeared (refers to water-processed sheets).

7. Attempts were made to explain the particularly pronounced effect of the stearoyl radical and the observation that the effect of the butyryl was closer to the effect of the stearoyl than to that of the acetyl.

8. Sheets of low hygroexpansivity and reasonable strength properties can be prepared from fibrous cellulose esters of acetic and butyric acids by processing in an organic medium.
REFERENCES CITED


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